

# A Novel Bis(azatitanatrane) with a T-Shaped Nitrido Bridging Ligand: Synthesis and Structure of $\{[N(CH_2CH_2N-i-Pr)_3Ti]_2(\mu_3-N)Na(THF)\}$

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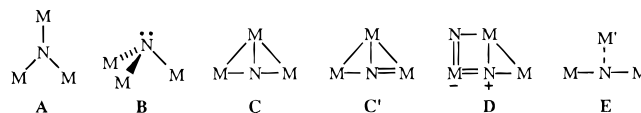
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The title compound **1** was unexpectedly synthesized by the reaction of  $CITi(i-PrNCH_2CH_2)_3N$  and excess  $NaNH_2$  in THF. A single-crystal X-ray diffraction study of **1** revealed that two azatitanatrane units and a sodium atom are bridged by a T-shaped nitrido ligand, the first such structure unsupported by a metal–metal bond. Structural evidence is presented for substantial  $\pi$  bonding in the TiN(nitrido)Ti bridging linkages that at least partially accounts for the unexpectedly long sodium–nitrido distance.

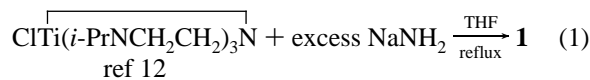
## Introduction

Nitrido transition metal complexes are gaining attention because of their diverse chemistry, their role in catalytic reactions, and their usefulness and potential usefulness as tumor, heart, and brain imaging agents and their interest as subjects of theoretical studies.<sup>1–5</sup> Nitrido complexes can include one or more transition metals with a variety of coordination numbers. It is quite common for a nitrido ligand to act as a terminal<sup>1–6</sup> or a  $\mu_2$ -bridging<sup>1–5,7</sup> ligand, although compounds with a nitrido ligand linking three,<sup>1,8</sup> four,<sup>9,10</sup> five,<sup>10</sup> and six<sup>11</sup> metal atoms have also been reported. Nitrido ligands in group 4 metal complexes are extremely rare. To our knowledge, there are only two reports of nitrido titanium complexes, namely,  $[\{\eta^5-C_5Me_5\}Ti(NH)_3N]$ ,<sup>8b</sup> and  $[\{\eta^5-C_5Me_5\}_4(\mu_3-N)_4]$ ,<sup>8g</sup> in which the pyramidal nitrido ligand bridges all three metals. Heretofore,

compounds containing  $\mu_3$ -bridging nitrido ligands have fallen into the four structural types shown below as **A** (trigonal planar),<sup>8c</sup> **B** (pyramidal),<sup>8b</sup> **C** and **C'** (T-shaped cluster), and **D** (a T-shaped nitrido cluster with one arm bridged by a second



nitrido ligand).<sup>8a</sup> Here we report the accidental synthesis of  $\{[N(CH_2CH_2N-i-Pr)_3Ti]_2(\mu_3-N)Na(THF)\}$ , **1**, an example of a T-shaped nitrido system unsupported by a metal–metal bond and the first member of the new structural class **E** in which one of the metals is a main group metal loosely bound to the nitrogen. Compound **1** was obtained in reaction 1 during an



attempt to synthesize  $H_2NTi(i-PrNCH_2CH_2)_3N$ , **2**,<sup>13</sup> since a similar route was successfully utilized to produce  $Me_2NTi(Me_3SiNCH_2CH_2)_3N$ .<sup>14</sup> Although the pathway followed in reaction 1 is not known, a plausible route is proposed in Scheme 1. The primary driving force in this sequence of reactions appears to

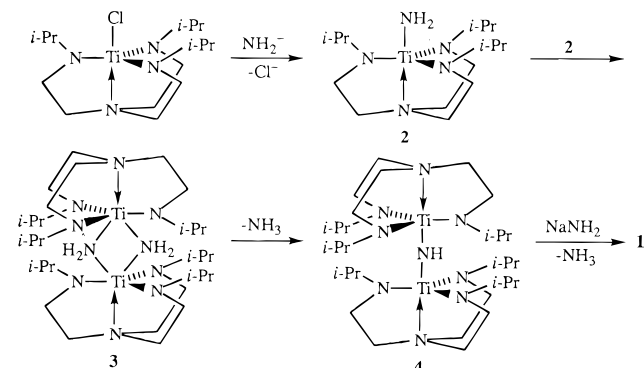
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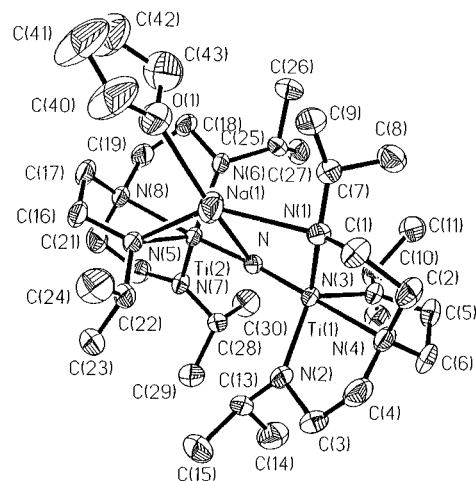
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## Scheme 1



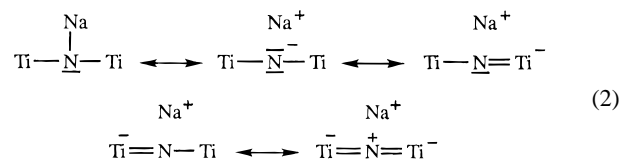
be the release of gaseous  $\text{NH}_3$  which was detected in the cold trap through which the argon used to blanket the reaction was passed. The putative intermediate **4** is likely to possess a virtually linear  $\text{C}_3$  axis owing to steric strain encountered during rehybridization of the nitrido nitrogen toward  $\text{sp}^2$  to more tightly bond the proton. The last step in Scheme 1 apparently occurs despite the electron-rich and sterically protected nature of the imido nitrogen in the proposed intermediate **4**. The electron richness of the imido nitrogen (owing to the presence of two  $\text{N}\text{--Ti}$  transannular bonds) would tend to bind the  $\text{NH}$  hydrogen more tightly to a nitrido  $p$  orbital. On the other hand, a multiply bonded resonance structure in the nitrido–titanium linkages ( $\text{Ti}^-\text{=N}^+\text{=Ti}^-$  in the extreme) in **4** would countervail the transannular bonding effect, rendering the imido hydrogen more protonic and therefore more vulnerable to abstraction by  $\text{NH}_2^-$  by a dissociative mechanism. The sole evidence for the pathway in Scheme 1 is the detection of a peak corresponding to the mass of **2** +  $\text{H}^+$  in the CI mass spectrum of **1** and also in its EI mass spectrum wherein self-ionization probably occurs.

Evidence for  $\pi$  bonding in the nitrido bridging bonds in **4** comes from the structure of **1** determined by X-ray means (Figure 1).<sup>15</sup> The three metal atoms and the nitrido ligand form a T-shape in this structure with a mean deviation from the plane of the T of 0.0268 Å. The  $\text{Ti}(1)\text{--N--Ti}(2)$  axis is distorted from linearity by only  $5.5^\circ$ . The  $\text{Ti}(1)\text{--N}$  and  $\text{Ti}(2)\text{--N}$  bond lengths (1.828(4) and 1.836(4) Å, respectively) are within  $3\sigma$  of one another and their average (1.832(4) Å) is shorter than that in the aforementioned complex  $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{NH})_3\text{N}]\}$  (1.913(7) Å)<sup>8b</sup> in which the nitrido ligand is pyramidal, thus promoting the formation of a single  $\text{Ti}\text{--N}$  bond length which has been calculated to be 1.981 Å.<sup>16</sup> By contrast the nitrido–titanium bond lengths in **1** are comparable to the imido–titanium distances in  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{NPPH}_3]$  (1.78(1) Å),<sup>17a</sup>  $\text{Ph}_2\text{P}(\text{S})\text{NTiCl}_2\cdot 3\text{py}$  (1.720(2) Å),<sup>17b</sup> and  $\text{Cl}_3\text{TiNPPH}_3$  (1.719–(4) Å)<sup>17c</sup> which possess substantial  $\text{Ti}\text{--N}$  double bond character. Consistent with the same notion for **1** is its sodium–nitrido bond length ( $\text{Na}(\text{CN}4)\text{--N}(\text{CN}3)$ , 2.589(5) Å) which not only is the

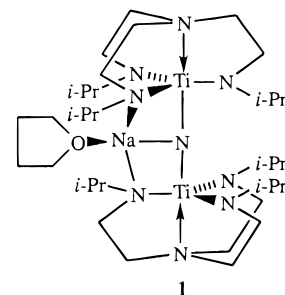


**Figure 1.** ORTEP drawing of **1** with atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

longest of the three  $\text{Na}\text{--N}$  bond lengths in this compound (Figure 1) but also is longer than the shortest  $\text{Na}(\text{CN}4)\text{--N}(\text{CN}4)$  length (2.35 Å) and comparable to the longest  $\text{Na}(\text{CN}4)\text{--N}(\text{CN}6)$  distance (2.60 Å) found in decameric and dodecameric sodium amides ( $\text{CN}$  = coordination number).<sup>18</sup> Thus it would appear that the last resonance structure of the five shown in eq 2 is most influential in determining the metrics in **1**, and it is



perhaps also responsible for permitting the conversion of **4** to **1**. The nearly staggered arrangement of the azatitanatranes in **1** shown in an idealized rendering of Figure 1 (torsion



angles of  $-62.3^\circ$  for  $\text{N}(1)\text{Ti}(1)\text{Ti}(2)\text{N}(5)$ ,  $+58.1^\circ$  for  $\text{N}(1)\text{Ti}(1)\text{Ti}(2)\text{N}(6)$ , and  $-179.4^\circ$  for  $\text{N}(1)\text{Ti}(1)\text{Ti}(2)\text{N}(7)$  could allow the sodium to be chelated by up to four nitrogens. The two ligated amino nitrogens, the ligated oxygen, and the sodium atoms all lie in the same plane (mean deviation 0.0313 Å) while the nitrido ligand lies 1.01 Å above this plane and 2.589(5) Å from the sodium. As with other structured monomeric azatitanatranes,<sup>12,14,18</sup> each titanium in **1** has a slightly distorted  $\text{tbp}$  geometry with protrusions of the metal atoms from the surrounding plane of three amido nitrogens an average of 0.440 Å in the direction of the nitrido ligand. The  $\text{N}\text{--Ti}$  transannular

- (13) A 100 mL Schlenk flask was charged with 0.73 g (2.1 mmol) of  $\text{ClTi}(\text{i-PrNCH}_2\text{CH}_2)_3\text{N}$  and 0.14 g (95%, 3.4 mmol) of  $\text{NaNH}_2$ . To these reactants was added 50 mL of THF under argon, and the reaction mixture was refluxed for 134 h. After the reaction was cooled, the volatile components were removed *in vacuo* and the residue was extracted with copious amounts of pentane. The extract was concentrated to about 5 mL and kept in a freezer for 1 day, which allowed red-orange crystals to form. After filtration at  $-50^\circ\text{C}$  and washing with cold pentane, 0.36 g of crystalline **1** was obtained in 46% yield.
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- (15) Red-orange crystals orthorhombic, space group  $Pbca$ ,  $a = 21.106(7)$  Å,  $b = 17.261(5)$  Å,  $c = 22.835(8)$  Å,  $V = 8319(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $R = 5.05\%$ ,  $\text{GOF} = 0.83$ .
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bonds in **1** (average 2.318(4) Å) lie between those determined for  $\text{Me}_2\text{NTi}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$  (2.257(2) Å)<sup>19</sup> and  $\text{Me}_3\text{SiO-Ti}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$  (2.451(5) Å).<sup>14</sup> That  $\pi$  bonding of the axial  $\text{Me}_2\text{N}$  and  $\text{Me}_3\text{SiO}$  groups to titanium is also operative in the latter compounds is suggested by the virtually trigonal planar (sum of angles = 358.3(2)°) and linear (176.0(2)°) coordination geometries of the nitrogen and oxygen atoms in these axial groups, respectively.

In contrast to the solid state structure, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** in solution reveal  $C_{3v}$  symmetry, due to rapid rotation on the NMR time scale of each tricyclic azatitanatrane around the N(8)–Ti(2)–N–Ti(1)–N(4) axis.

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**Supporting Information Available:** Text giving characterization data and the procedure used for the structure determination, tables giving crystal data and details of the structure determination, atomic coordinates, bond lengths, bond angles, and isotropic and anisotropic thermal parameters, and a packing diagram for **1** (26 pages). See any current masthead page for ordering information and Internet access instructions.

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