A Nitrido Salt Reagent of Titanium

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Ⓢ *Supporting Information*

ABSTRACT: Deprotonation of the parent titanium imido $(^{tBu}nacnac)Ti\equiv NH(Ntolyl_2)$ $(^{tBu}nacnac^- = [ArNC^tBu]_2CH; Ar = 2,6-^iPr_2C_6H_3)$ with KCH_2Ph forms a rare example of a molecular titanium nitride as a dimer, $\{[K][(^{tBu}nacnac)Ti\equiv N(Ntolyl_2)]\}_2$. From the parent imido or nitride salt, the corresponding aluminylimido–etherate adduct, $(^{tBu}nacnac)Ti\equiv N[AlMe_2(OEt_2)]-(Ntolyl_2)$, can be isolated and structurally characterized. The parent imido is also a source for the related borylimido, $(^{tBu}nacnac)Ti\equiv NBEt_2(Ntolyl_2)$.

Because of the large difference in electronegativity and consequentially the polarization of the metal−nitrogen bond, titanium complexes possessing a terminal nitride ligand remain elusive.[1] To date, the only documented examples of mononuclear titanium nitrides are those reported by Lancaster and co-workers, in which the nitride functionality is protected by a borane group,[2−4] rendering them somewhat inert to further reactivity. We recently reported a rare example of a four-coordinate parent titanium imido complex, $(^{Me}nacnac)Ti\equiv NH(Ntolyl_2)$ $(^{Me}nacnac^- = [ArNCMe]_2CH; Ar = 2,6-^iPr_2C_6H_3)$;[5] however, all attempts to deprotonate the imido ligand resulted instead in deprotonation of the β-methyl backbone of the β-diketiminate ligand. This transformation has precedent and is attributed to the ligand's propensity to tautomerize to the tethered bisanilide species.[6−9] For this reason, we focused our attention toward preparing an analogous parent titanium imido having the more sterically encumbering and robust *tert*-butyl-substituted ligand $^{tBu}nacnac$ $(^{tBu}nacnac^- = [ArNC^tBu]_2CH; Ar = 2,6-^iPr_2C_6H_3)$.[10,11] In this work, we showcase spectroscopic and structural evidence for the first molecular titanium nitride salt and its reactivity in the form of a terminal nitride. We also demonstrate that in addition to being a precursor to the nitride ligand, the parent imido is a convenient template for rare imido scaffolds.

The compound $(^{tBu}nacnac)TiCl(Ntolyl_2)$ (**1**) was prepared in 74% yield via transmetalation of $(^{tBu}nacnac)TiCl_2$[12] with $LiNtolyl_2$ (Scheme 1).[13,14] Complex **1** displays characteristic features of a d[1] species (Evans method: $\mu_{eff} = 1.82\mu_B$, 25 °C, C_6D_6), while the room-temperature X-band EPR spectrum shows features similar to those of the analogue $(^{Me}nacnac)TiCl(Ntolyl_2)$[5] ($g_{iso} = 1.96$, $W = 5$ G, toluene). A solid-state structure also confirmed the formation of a mononuclear, four-coordinate Ti(III) species (Figure 1). Likely as a result of the increased steric bulk of the $^{tBu}nacnac$ ligand, the $Ntolyl_2$

Scheme 1. Synthetic Protocol for the Parent Imido 2 and Nitride 3
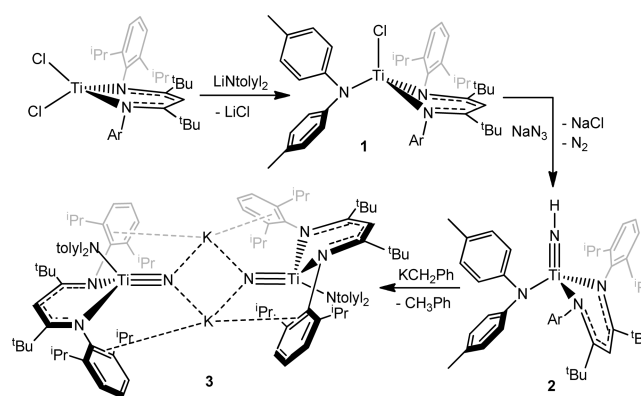
titanium−nitrogen distance increased from 2.016(2) Å in the $^{Me}nacnac$ analogue to 2.071(1) Å in **1**. Following a protocol similar to that for the parent imido $(^{Me}nacnac)Ti\equiv NH(Ntolyl_2)$,[5] treatment of **1** with a slight excess of NaN_3 in THF resulted in a gradual color change from olive green to yellow-orange.[14] Workup of the reaction mixture and recrystallization of the yellow precipitate resulted in isolation of the terminal parent imido $(^{tBu}nacnac)Ti\equiv NH-(Ntolyl_2)$ (**2**) in 45% yield (Scheme 1).[14] ^{1}H NMR spectroscopic data revealed a C_s-symmetric molecule with one ^tBu environment, as well as two locked ^iPr and tolyl groups on the *N*-aryl and $Ntolyl_2$ moieties, respectively. A broad feature at 3.86 ppm in the ^{1}H NMR spectrum is consistent with the terminal N*H* resonance, and preparation of the isotopomer $(^{tBu}nacnac)Ti\equiv^{15}NH(Ntolyl_2)$ (**2**-^{15}N) using 98%-enriched $Na^{15}N_3$ resolved nearly 50% of the broad feature into a doublet centered at 3.86 ppm with a $^1J_{NH}$ value of 64 Hz. An INEPT ^{15}N{^{1}H} NMR spectrum of **2**-^{15}N evinced a sharp resonance at 421 ppm with an identical $^1J_{NH}$ value.[14] Lastly, the solid-state IR (Nujol) spectrum of **2** displayed a sharp stretch at 3397 cm^{−1}, while **2**-^{15}N showed a red-shifted stretch at 3390 cm^{−1}, in good agreement with the difference predicted by the harmonic oscillator model ($\Delta = 8$ cm[−1]).[14] X-ray diffraction studies on yellow crystals of **2** further corroborated our assessment of this species as mononuclear and thus possessing a rare example of a terminal NH ligand (Figure 1).[15] In the solid-state structure of **2**, the imido Ti−N distance [Ti1−N4 = 1.6917(15) Å] is
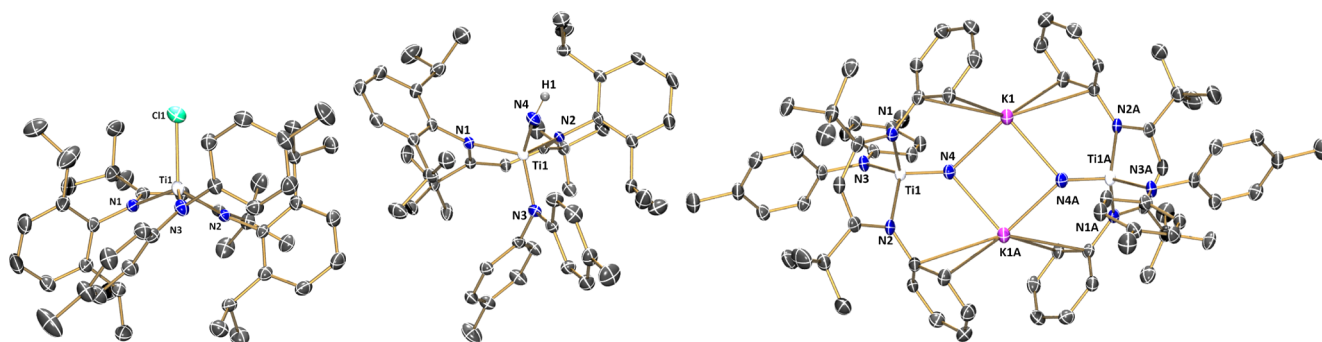
Figure 1. Solid-state structures of complexes **1**−**3** displaying thermal ellipsoids at the 50% probability level. All hydrogens (with exception of the imido H in **2**) and solvent molecules have been omitted for clarity. The isopropyl groups on **3** have also been omitted for clarity.

slightly longer than that in the related ^{Me}nacnac species [1.6885(14) Å]. Additionally, the N−H proton was located in the difference map and refined isotropically. Interestingly, oxidation of the Ti center in **1** to the d^0 species **2** resulted in substantial twisting of the anilide ligand to an up−down conformation that allows for optimal π donation by the Ntolyl$_2$ lone pair to the metal center. This was also corroborated by a 0.09 Å contraction of the Ti1−N3 distance in **2** compared with **1**.

To assess whether the solvent is the H-atom source in the formation of **2**, the synthesis of the isotopomer (^{tBu}nacnac)-Ti≡ND(Ntolyl$_2$) (**2-d_1**) in THF-d_8 was attempted. The IR spectrum of the resulting product revealed no sign of an N−D stretching frequency. Disappointingly, traditional H-atom sources such as 1,4-cyclohexadiene and 9,10-dihydroanthracene did not lead to improved yields of **2**, suggesting the source of this atom to be ligand-based (hence resulting in a yield of less than 50%). Therefore, we speculate at this time that the source of the H atom must derive from degradation of the ^{tBu}nacnac or Ntolyl$_2$ ancillaries.

Complex **2** reacts cleanly with benzylpotassium in toluene to afford a poorly soluble crystalline product along with toluene (detected by ^{1}H NMR spectroscopy). The ^{1}H NMR spectrum of this new material is characteristic of a similar C_s-symmetric species with the two aryl rings of the Ntolyl$_2$ group still locked in place, consistent with formation of a nitride having the formula "[K][(^{tBu}nacnac)Ti(N)(Ntolyl$_2$)]". The most salient change in the ^{1}H NMR spectrum is the disappearance of the broad parent imido (Ti≡N*H*) resonance centered at 3.86 ppm. Likewise, the doublet ^{1}H NMR resonance for **2-^{15}N** was also absent after this species was treated with benzylpotassium.[14] Despite several attempts, no signal was observed in the solution-state ^{15}N NMR spectrum, which we attribute to the low solubility of the "[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]" salt in most common nonprotic organic solvents in addition to the low NMR sensitivity of the ^{15}N nucleus (~0.1% as sensitive as ^{1}H). To circumvent this limitation, we acquired solid-state ^{15}N NMR spectra to further characterize the Ti−N bonding in this insoluble product.[14] Gratifyingly, the ^{15}N NMR signal for the ^{15}N-enriched nitrido ligand in "[K][(^{tBu}nacnac)Ti≡^{15}N-(Ntolyl$_2$)]" is highly deshielded [δ_{iso} = 898(2) ppm] and also exhibits an exceedingly large chemical shift anisotropy spanning a range of over 1000 ppm [δ_{11} = 1353(50), δ_{22} = 1143(50), δ_{33} = 198(50) ppm; Figure 2]. The highly deshielded resonance, albeit in the solid-state, is comparable to those of neutral vanadium nitrides having similar scaffolds, namely, [(^{Me}nacnac)V≡N(X)] [X = N(mesityl)(tolyl), Ntolyl$_2$, and
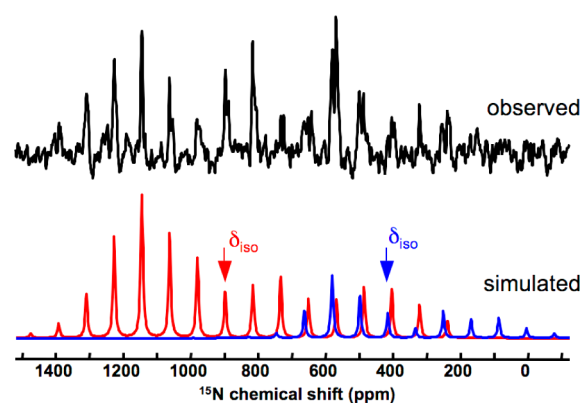

Figure 2. Solid-state ^{15}N NMR spectrum of **3** (black) and simulated spectra of **3** (red) and **2** (blue) overlaid.

OAr].[13,17] The observed ^{15}N chemical shift tensor parameters are characteristic of a terminal metal−ligand triple bond, as previously noted in terminally bound molybdenum nitride, phosphide, and carbide compounds.[16] For example, the ^{15}N chemical shift tensor for ^{15}N≡Mo(N[^{t}Bu]Ar′)$_3$ (Ar′ = 3,5-Me$_2$C$_6$H$_3$) is δ_{iso} = 833 ppm, δ_{11} = δ_{22} = 1229 ppm, and δ_{33} = 42 ppm. Interestingly, the ^{15}N chemical shift tensor in "[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]" deviates considerably from axial symmetry [$\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33}) = 0.64$], and this feature can be attributed to the fact that the Ti center in "[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]" does not possess a C_3-symmetric environment, inasmuch as the nitrido atom is further involved in interactions with K$^+$ cations. This latter structural feature in "[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]" is also similar to that observed in the isovalent Mo−carbido having two bridging K$^+$, {[K][(^{13}C≡MoN[^{t}Bu]Ar)$_3$]}$_2$, for which the ^{13}C chemical shift tensor is also nonaxially symmetric (κ = 0.88).[16c] For completeness, the ^{15}N chemical shift tensor for ^{15}N-enriched **2** (**2-^{15}N**) was also determined: δ_{iso} = 416(2) ppm, δ_{11} = δ_{22} = 656(50), δ_{33} = −64(50) ppm. Once again, the general features of this ^{15}N chemical shift tensor for the Ti≡^{15}NH moiety in **2-^{15}N** are analogous to those of the ^{13}C chemical shift tensor reported for H^{13}C≡Mo(N[^{t}Bu]Ar)$_3$,[16c] in accord with a triple-bonded ligand.

To conclusively establish the connectivity of this salt-like material and to ascertain the degree of aggregation in "[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]" we collected X-ray diffraction data on a single crystal grown rapidly from Et$_2$O at −37 °C. Scheme 1 and Figure 1 portray two titanium nitride fragments, [(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]$^-$, bridged by two K$^+$ ions, labeled as compound {[K][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)]}$_2$

(**3**). The most notable feature is the short titanium−nitride distance of 1.660(4) Å, which is slightly shorter than that in the $B(C_6F_5)_3$-protected titanium nitrides reported by Lancaster and co-workers (1.671 Å).[2−4] The K_2N_2 core forms a perfect diamond shape (sum of the four angles = 360°) while the K^+ interacts with the π components (mostly the ipso and ortho positions) of the aryl moieties of the β-diketiminate ligand.

Interestingly, the use of $NaHBEt_3$ as an alternative base with **2** resulted in neither **3** nor a hypothetical borane-capped nitride salt "[Na][(^{tBu}nacnac)Ti≡NBEt$_3$(Ntolyl$_2$)]" but rather showed conversion to the borylimido complex (^{tBu}nacnac)-Ti=NBEt$_2$(Ntolyl$_2$) (**4**) in addition to H_2 (Scheme 2). The

Scheme 2. Convergent Synthesis of the First Boryl and Aluminyl Imidos of Group 4 Transition Metals Using Either Nitride 3 or the Parent Imide
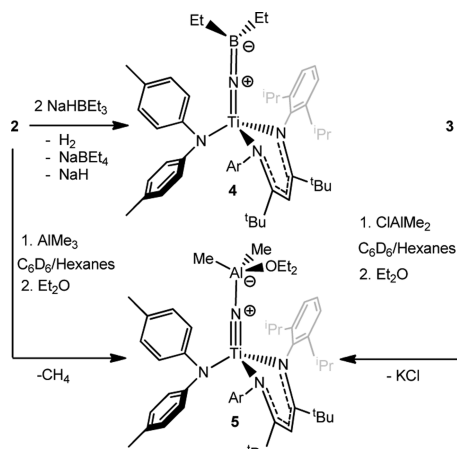
use of 2 equiv of $NaHBEt_3$ was required in order to drive the reaction to completion as well as the formation of precipitates. ^1H NMR spectroscopy of the crude mixture showed no evidence of salt biproducts such as NaEt, but this is not surprising given its poor solubility in nonpolar solvents.[18] Furthermore, ethane or ethylene were not detected by ^1H NMR spectroscopy, suggesting that an ethyl radical pathway is not likely. However, the ^{11}B NMR spectrum of the crude mixture was more informative, displaying a resonance at −13 ppm which we tentatively assign as $NaBEt_4$;[19] the relative instability of this anion is also shown by the presence of a second ^{11}B resonance at 86 ppm, which corresponds to BEt_3.[14] The ^1H and ^{13}C NMR spectra of **4** reveal an overall geometry akin to that of parent imido **2**. Notably, the solid-state structure of **4** (Figure 3) depicts a tetrahedral titanium complex having a terminal linear borylimido [Ti=N, 1.722(3) Å; N=B, 1.428(6) Å; Ti−N−B, 168.1(3)°], in accord with a delocalized π Ti=N=B topology. Early transition metal borylimidos are extremely rare,[20] and complex **4** represents the first example involving a group 4 transition metal. The formation of **4** is also intriguing because the B−N bond results from the breaking of a very strong B−C bond (bond dissociation energy = 107.1 kcal/mol). We found that direct addition of BEt_3 to **3** did not afford **4**, suggesting that **4** does not result from thermal decomposition of a putative [Na][(^{tBu}nacnac)Ti≡NBEt$_3$(Ntolyl$_2$)] species. This result also argues that the second equivalent of $NaHBEt_3$ is indispensable in the formation of **4**.

Intrigued by the ability of **2** to function as a nitride synthon, we reacted this species with $AlMe_3$ to readily eliminate methane gas (observed by ^1H NMR spectroscopy), forming a dark-
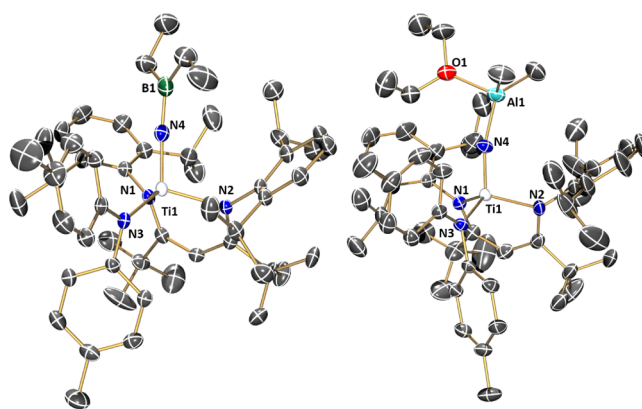
Figure 3. Solid-state structures of complexes **4** and **5** depicting thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

orange precipitate that is poorly soluble in arenes. Slow evaporation of a concentrated Et_2O solution of this complex led to the formation of yellow-green dichroic crystals of the aluminylimido−etherate adduct (^{tBu}nacnac)Ti≡N-[AlMe$_2$(OEt$_2$)](Ntolyl$_2$) (**5**) (Scheme 2). Compound **5** is also C_s-symmetric in solution as gauged by ^1H NMR spectroscopy, which revealed a single methyl resonance at −0.925 ppm as well as broad Et_2O resonances at 0.594 and 3.05 ppm. The ^{27}Al NMR spectrum of **5** exhibits a very broad signal located at ∼191 pm, confirming the Al to be four-coordinate in solution.[14]

The solid-state structure of **5** (Figure 3) divulges a linear Ti−N−Al moiety [166.34(14)°] containing a short Ti−N bond [1.6922(19) Å], again indicative of multiple-bond character, while the Al−N distance [1.834(2) Å] is more in accord with a single bond as a result of coordination of a molecule of Et_2O. Furthermore, the Al−Me bond lengths [1.961(4) and 1.969(3) Å] are not significantly elongated relative to an average Al−Me bond, also signifying little hyperconjugation with the imido π system. The geometry around the aluminum can be considered as distorted tetrahedral, with the most acute angle being the N4−Al1−O1 angle [98.48(10)] because of the longer Al−O dative bond [1.960(2) Å]. To the best of our knowledge, complex **5** constitutes the first example of a transition metal having a terminally bound aluminylimido ligand. Recognizing that the nitride salt could undergo salt elimination reactions to afford the same product, we added a dilute solution of $AlMe_2Cl$ in hexanes to a benzene solution of **3**, which resulted in the formation of the same poorly soluble orange product, presumably "(^{tBu}nacnac)Ti≡N[AlMe$_2$](Ntolyl$_2$)", which upon exposure to Et_2O yielded **5**, as gauged by ^1H NMR spectroscopy.

While compound **3** is partially soluble and stable in both Et_2O and DME for several hours, the presence of THF rapidly decomposes this nitride to a dark-orange compound of much lower symmetry based on ^1H NMR. Similarly, attempts to encapsulate the K^+ of **3** by forming the discrete salt [K(2,2,2-Cryptand)][(^{tBu}nacnac)Ti≡N(Ntolyl$_2$)] (2,2,2-Cryptand = 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8,8,8]hexacosane) failed under various conditions, instead resulting in what we propose to be intramolecular cross-metathesis rearrangements involving the β-diketiminate scaffold and the nitride (among other products). We have observed similar metathesis transformations of nacnac with nitride, alkylidyne, and alkylidene ligands.[13,17,21]

In conclusion, we have shown that as a result of a modification of the nacnac ligand, deprotonation of a parent titanium imido leads to the formation of the first molecular titanium nitride salt and that this species serves as a source of a terminal nitride. Likewise, we confirmed that the parent imido **2** may be used as a complementary nitride synthon, taking advantage of the vulnerable N–H bond.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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