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A Nitrido Salt Reagent of Titanium

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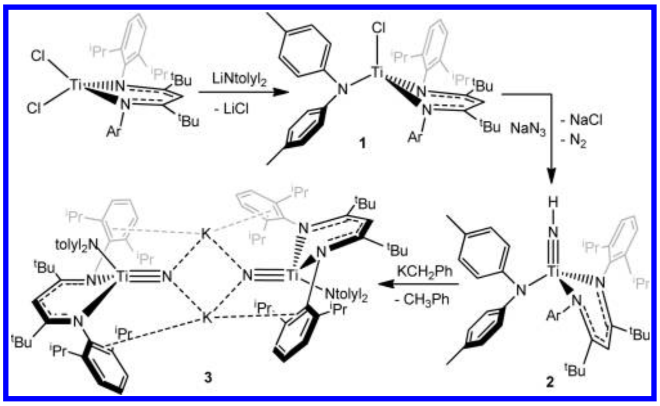
Supporting Information

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, $(^{tBu}nacnac)Ti{=}NBEt_2(Ntolyl_2)$.

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.

Scheme 1. Synthetic Protocol for the Parent Imido 2 and Nitride 3



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: μ_{eff} = 1.82μ_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 $Ntolyl_2$ 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] ^1H 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 ^1H NMR spectrum is consistent with the terminal *NH* 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 $^{15}N\{^1H\}$ 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 (Δ = 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

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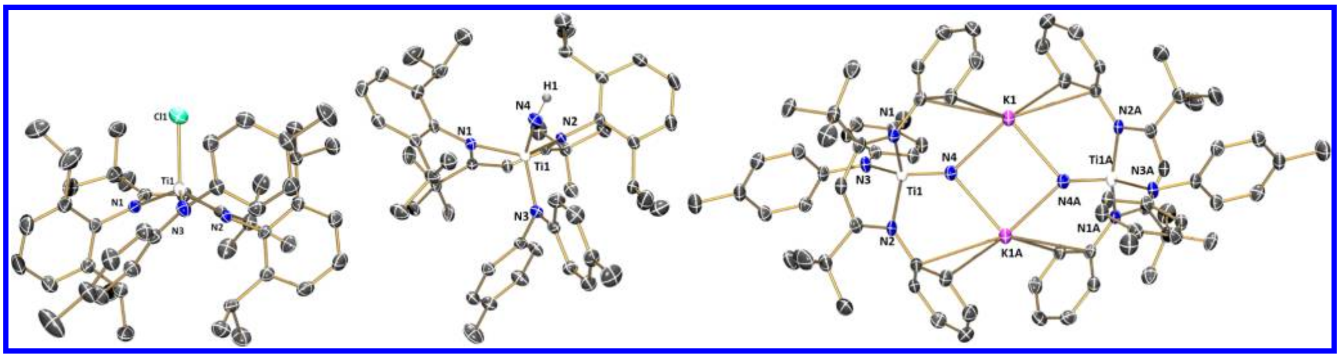


Figure 1. Solid-state structures of complexes **1**−**3** displaying thermal ellipsoids at the 50% probability level. All hydrogens (with exception of the imido H in **2**) and solvent molecules have been omitted for clarity. The isopropyl groups on **3** have also been omitted for clarity.

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 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.

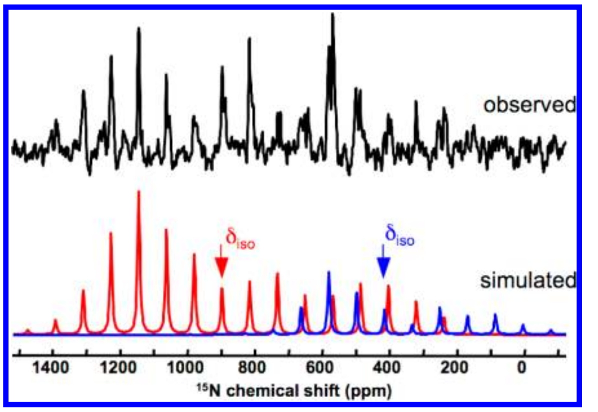


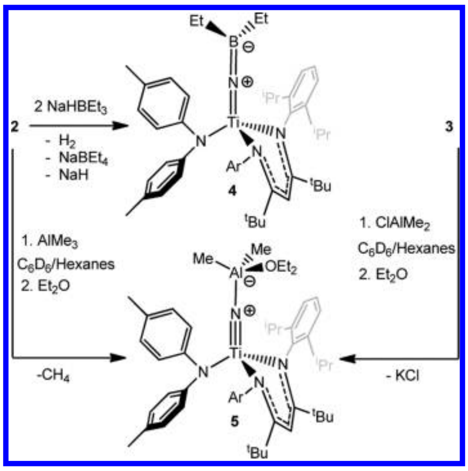
Figure 2. Solid-state ^{15}N NMR spectrum of **3** (black) and simulated spectra of **3** (red) and **2** (blue) overlaid.

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 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**.

Scheme 2. Convergent Synthesis of the First Boryl and Aluminyl Imidos of Group 4 Transition Metals Using Either Nitride 3 or the Parent Imide



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-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]

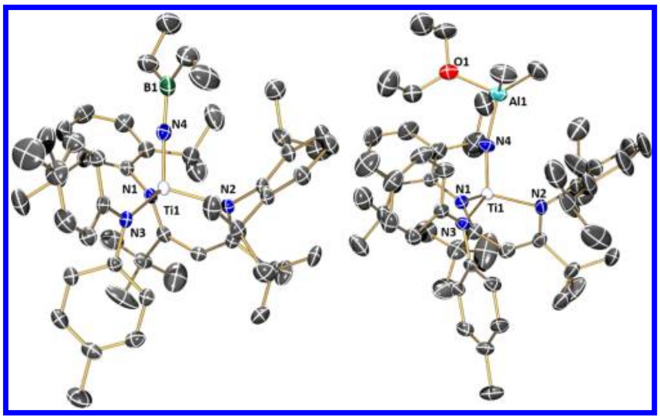


Figure 3. Solid-state structures of complexes **4** and **5** depicting thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

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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