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A four coordinate parent imide *via* a titanium nitridyl†‡

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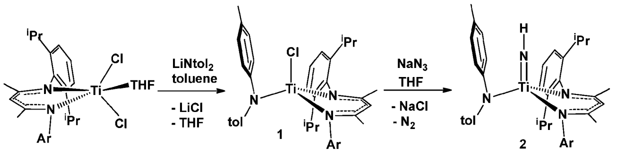
Treatment of d^1 [(nacnac)TiCl($Ntol_2$)] with NaN_3 results in NaCl formation and N_2 ejection to yield the first four coordinate, parent imide [(nacnac)Ti═NH($Ntol_2$)] ($nacnac^-$═[ArNC(CH_3)]$_2$-CH, Ar = 2,6-*i*$Pr_2C_6H_3$, tol = 4-$CH_3C_6H_4$).

Parent imides of titanium, [L_nTi═NH], are rare entities which is rather surprising given their presumed involvement in industrially important processes such as the fabrication of thin metal nitride films (*via* MOCVD methods).[1,2] Likewise, parent imides are intermediates in the Chatt-cycle involved in the generation of NH_3 from N_2, protons and electrons,[3] hence playing an important role enroute to molecular metal nitrides. To date, the only example of a terminal parent imide of titanium (or a group 4 transition metal) is the complex [$(Ph_3PO)_2$Ti═NH$(Cl)_2$] reported by Winter and co-workers.[4] Even though the imide functionality is now a common ligand in titanium chemistry,[5] the parent imide is not because of the lack of suitable reagents to incorporate the NH group.[5] Unlike metal nitrenes, which are often supported by electron rich metal centers,[6] we present in this work the metal nitridyl: an electron deficient nitride monoradical ligand supported by an electron deficient metal center.[7–9] The nitridyl moiety, $L_nM{=}\dot{N}{:} \leftrightarrow L_nM{\equiv}N^\bullet$, is an exceedingly rare functional group in part because of its reactivity at the electron deficient N-atom as well as accessibility from suitable precursors. Entry to a terminal nitride radical ligand has been seldom reported, involving either an outer-sphere one-electron oxidation of a nitride anion,[7–9] or one-electron reduction of a N-atom source such as an azide, N_3^-.[9]

We recently reported the unsaturated vanadium nitrides, [(nacnac)V≡N(N[tol]R′)] (tol = 4-MeC_6H_4; R′ = tol or 2,4,6-$Me_3C_6H_2$), by treatment of the V(III) precursor [(nacnac)VCl(N[tol]R′)] with NaN_3, followed by N_2 extrusion from the metastable azide [(nacnac)V(N_3)(N[tol]R′)].[10] Being one electron shy of [(nacnac)VCl(N[tol]R′)], it was envisioned that treatment of a similar Ti(III) precursor with NaN_3 should incorporate a reactive and unprecendented nitridyl moiety of titanium [(nacnac)Ti($N^\bullet$)($Ntol_2$)] *via* the entropy driven loss of nitrogen. Accordingly, transmetallation of [(nacnac)-$TiCl_2$(THF)][11] with $LiNtol_2$ in toluene readily forms the titanium precursor [(nacnac)TiCl($Ntol_2$)] (**1**) in 60% yield as dark green colored crystals after recrystallization from diethyl ether at −37 °C (Scheme 1).[12] Replacing a Cl^- with $Ntol_2^-$ ligand provides steric protection at the metal center in a tetrahedral environment and also restricts salt elimination at only one Cl^- ligand given the poor solubility of NaN_3 in most common organic solvents. Complex **1** shows characteristic features of a d^1 species by the method of Evans (μ_{eff} = 1.89 μ_B, 25 °C, C_6D_6), and by an isotropic X-band EPR spectrum collected at room temperature (g_{iso} = 1.95, *W* = 45 G, toluene).[12] A solid state structure of **1**§ provides the connectivity of this radical and reveals a pseudo-tetrahedral complex reminiscent to the related structure of [(nacnac)VCl($Ntol_2$)].[10] The molecular structure of **1** also displays a Ti atom that deviates 0.6381(9) Å above the imaginary plane (N1,N2,N3) defined by the anilide and nacnac nitrogens (Fig. 1). The above and below positions of the tolyl fragments, with respect to the aforementioned plane, forces the flanking aryl groups of the nacnac ligand to be locked thereby providing a sterically protected pocket at the Ti(III) center.

Treatment of **1** with a slight excess of freshly purified NaN_3[12] gradually results in a color change from green to red with concurrent formation of a diagmagnetic material along with other side-products.[12] Workup of the reaction mixture and subsequent recrystallization of the orange precipitate allows for identification of this new diamagnetic species in 30% yield.[12] By ^1H NMR spectroscopy, only one methyl environment for the β-carbon of nacnac is observed, while two *i*Pr and tolyl environments are clearly identified for the locked "up and down" groups on the aryl and $Ntol_2$ moieties consistent with an intact (nacnac)Ti(IV)($Ntol_2$) skeleton having overall C_s symmetry in solution. Unfortunately, the third ligand (presumably a N*H* resonance or N based ligand) was



Scheme 1 Synthesis of complexes **1** and **2** from salt metathesis.

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‡ Electronic supplementary information (ESI) available: Complete synthetic details and spectroscopic characterization, including NMR spectroscopic data for complexes **1** and **2**. The molecular structure of compounds **1** and **2** have been deposited in the CCDC as 829540 and 829541. See DOI: 10.1039/c1cc14574f.

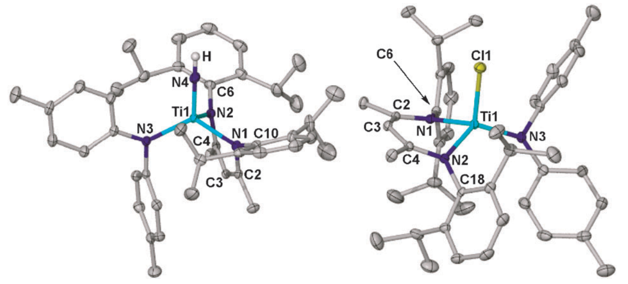


Fig. 1 Molecular structures of **1** (right) and **2** (left) shown with H-atoms (except for N4, complex **2**) have been excluded for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Ti–N(1), 2.037(4); Ti–N(2), 1.9995(4); Ti–N(3), 1.9577(4); Ti–Cl(1), 2.3234(3); N(1)–Ti–N(3), 124.67(19); N(1)–Ti–N(2), 90.99(17); N(1)–Ti–Cl(1), 105.82(19); N(3)–Ti–Cl(1), 111.77(19). For **2**: Ti–N(4), 1.688(4); Ti–N(2), 2.019(3); Ti–N(3), 2.016(4); N(4)–H, 0.880; Ti–N(1), 2.031(3); N(1)–Ti–N(2), 94.06(5); N(2)–Ti–N(3), 114.51(5); N(3)–Ti–N(4), 112.27(6); N(4)–Ti–N(1), 109.06(6); N(4)–Ti–N(2), 108.56(6); N(3)–Ti–N(1), 116.85(6).

not easily identified possibly due to coupling to quadrupolar ^{14}N. This feature is not uncommon, since Winter[4] and Schrock,[13] could not locate such resonance for the few reported titanium and vanadium complexes having a terminal parent imide ligand. Since our data provided inconclusive evidence for the parent imide ligand (or third ligand), we prepared the ^{15}N (from 98% enriched Na^{15}N$_3$ at one terminal nitrogen) isotopomer [(nacnac)Ti$=$^{15}NH(Ntol$_2$)] (**2**)-^{15}N (which contains ~ 50% of unlabeled **2**). The ^{15}N{^{1}H} NMR spectrum of **2**-^{15}N evinced a sharp resonance at 430 ppm with a $^1J_{\mathrm{NH}}$ value of 64 Hz (Fig. 2).[14] Moreover, the solid state IR (Nujol) spectrum of **2** displayed a sharp stretch at 3367 cm^{-1} while **2**-^{15}N showed two stretches for 50 : 50 mixture of **2** and **2**-^{15}N with the labeled compound red shifted to 3359 cm^{-1} (Fig. 2) in accord with the value predicted by the harmonic oscillator (3359 cm^{-1}). Careful analysis of the ^{1}H NMR spectrum of **2**-^{15}N revealed a doublet at 4.16 ppm with a $^1J_{\mathrm{HN}}$ value of 64 and a broad resonance, arising from ^{1}H-^{14}N coupling, sandwich between the doublet due to the presence of unlabeled **2** (Fig. 2). Applying an ^{15}N/^{1}H HSQC experiment, we could correlate the imido Ti$=$*N*H functionality to the broad resonance at 4.16 ppm (Fig. 2).

Although the IR and ^{15}N NMR spectroscopic data suggested **2** to contain a parent imide motif, we resorted to X-ray structural analysis of a small crystal using a synchrotron radiation source to conclusively establish the connectivity in **2**.¶ A perspective view of the solid state structure of **2** is shown in Fig. 1, along with selected bond lengths and angles, revealing a pseudo-tetrahedral complex whereby the nacnac and Ntol$_2$ basal ligands sterically protect the terminal parent imido group. Both the *i*Pr groups of the aryl moeities of nacnac as well as the tol groups, with respect to the (N1, N2, N3) plane, are in the upright position. The short Ti$=$N distance of 1.688(4) Å for the parent imide ligands lends support to a multiple bond, comparable to Winter's imide (1.627(8) Å)[4] but possibly having triple bond character analogous to the V$\equiv$N distance of the isoelectronic nitride [(nacnac)V$\equiv$N(N[tol]2,4,6-Me$_3$C$_6$H$_2$)] (1.573(2) Å),[10] as well as the Ti$\equiv$N distance of the zwitterionic titanium nitride borane adduct reported by Lancaster (1.671(3) Å).[15]

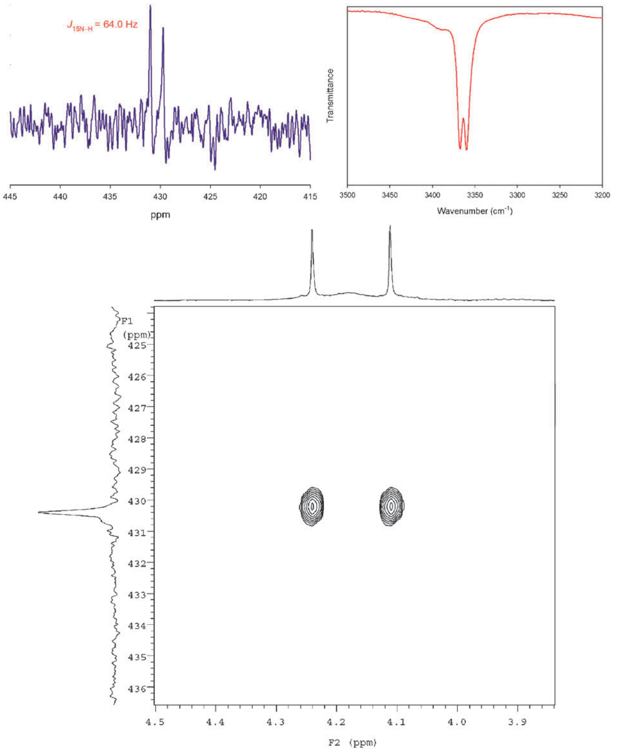
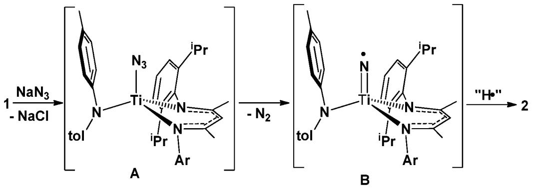


Fig. 2 (left) Expanded ^{15}N NMR spectrum of ^{15}N isotopmer of **2** showing ^{15}N–^{1}H coupling (left). Expanded FT-IR (Nujol) spectrum of **2**-^{15}N (right). Bottom figure is the HSQC NMR spectrum of **2**-^{15}N (^{15}N (vertical), ^{1}H (horizontal).

Formation of complex **2** from **1** and NaN$_3$ most likely involves salt elimination to form a titanium radical azide complex [(nacnac)Ti(N$_3$)(Ntol$_2$)] (**A**), which undergoes N$_2$ extrusion to form a transient nitridyl [(nacnac)Ti(N$^\bullet$)(Ntol$_2$)] (**B**) (Scheme 2). Although nitridyl radicals of this type are not observable, their formation is known to accompany ligand radical ejection, oligomerization, or H atom abstraction processes.[16] In our case, species **B** appears to abstract an H atom. To probe the origin of the H atom, we conducted a similar reaction of **1** and NaN$_3$ or Na^{15}N$_3$ in THF-d_8. In the case of unlabeled azide, formation of **2** is the only detectable species, whereas formation of [(nacnac)Ti$=$ND(Ntol$_2$)] is not evident by a combination of IR and ^{2}H NMR spectroscopies; therefore, implying that solvent *is not the source of hydrogen* to form **2**. Reacting **1** with Na^{15}N$_3$ in THF-d_8 also revealed formation of **2**-^{15}N without evidence for D-incorporation from the solvent as we clearly detected a doublet at 4.20 ppm for the Ti$=$^{15}N*H* moiety (*vide supra*). Based on this information, we propose H-atom abstraction to derive from the nacnac, Ntol$_2$ ligands, or even adventitious impurities present in the reaction mixture.



Scheme 2 Proposed mechanism to formation of complex **2** *via* azide (**A**) and nitridyl (**B**) intermediates.

The moderate yield of **2** and the spectroscopic observation of other side products by ^{1}H NMR spectroscopy of the crude reaction mixture imply H-atom abstraction to be non-selective. However, we cannot refute the possibility of some (albeit minor) H-atom abstraction from the solvent medium taking place or a large KIE resulting from deuteration of the solvent. Attempts for cleaner formation of **2** from the reaction of **1** and NaN_3 in 1,3-cyclohexadiene or 9,10-dihydroanthracene resulted in no improvement of the yield. Using N_3SiMe_3 with **1** also formed **2** in similar isolated yields (34%).[12]

Preliminary attempts to generate a titanium nitride anion by depromotonation of complex **2**-^{15}N using bases such as KH or KCH_2Ph in THF failed to remove the proton. Instead, a new product is produced in the reaction mixture based on multinuclear (^{15}N, ^{1}H) NMR spectroscopy. For example, the ^{15}N NMR spectrum displays a new doublet at 394 ppm ($^{1}J_{NH}$ = 58 Hz) indicative of retention of the NH group. Further analysis of the new product by ^{1}H NMR shows the ^{15}N–H resonance also as a doublet at 5.78 ppm ($^{1}J_{HN}$ = 58 Hz). As a result, we propose that deprotonation of the nacnac β-methyl group has occurred. This conclusion is corroborated by the loss of symmetry of the nacnac ligand: a singlet at 1.56 ppm integrated to 3H [(*Me*)C(NAr)CH(CH_2)(NAr)] and two different singlets at 3.12 and 2.46 ppm integrated to one H for each resonance and assigned to the geminal methylene group in $[(Me)C(NAr)CH(CH_2)(NAr)]^{2-}$.[17]

In this work, we have demonstrated that incomplete reduction of the N_3^- ligand by a d^1 metal center still results in N_2 extrusion with presumed formation of an electron deficient titanium nitridyl, thereby providing entry to a rare example of a group 4 parent imide. Rather than undergoing ligand radical ejection or N–N coupling to form an N_2^{4-} ligand, H-atom abstraction (not from solvent) appears to be the dominant pathway in formation the N–H bond. Current effort in our group is geared toward utilizing the *t*-butyl version of the nacnac scaffold, $[(^tBu)C(NAr)CH(^tBu)(NAr)]^-$, to circumvent the problem of backbone deprotonation.

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Notes and references

§ X-ray data for **1**: monoclinic, $P2_1/c$, T = 150(2)K a = 10.6177(10), b = 33.391(3), c = 11.5326(11), β = 107.582(2)°, Z = 4, V = 3897.7(6) Å^3, absorption coefficient = 0.321, F(000) = 1492, θ range (deg) = 0.1.95–27.60, no. of reflections collected = 39483, no. of unique reflections = 9003, data/parameter ratio = 18.83, $R(F)$ = 0.0439, $R_w(F^2)$ = 0.0985, GOF = 1.034, largest diff. peak and hole = 0.362 and −0.329.

¶ X-ray data for **2**: monoclinic, $P2_1/c$, T = 120(2)K, a = 11.(9), b = 28.874(2), c = 12.3682(9), β = 115.276(2)°, Z = 4, V = 3806.5(5) Å^3, absorption coefficient = 0.142, F(000) = 1456, θ range (deg) = 0.82 – 18.54, no. of reflections collected = 85 507, no. of unique reflections = 14 417, data/parameter ratio = 32.39, $R(F)$ = 0.0535, $R_w(F^2)$ = 0.1017, GOF = 1.040, largest diff. peak and hole = 0.953 and −1.002.

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