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Snapshots of an oxidatively induced α-hydrogen abstraction reaction to prepare a terminal and four-coordinate titanium imide†

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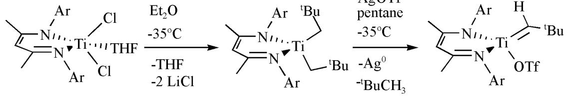
One electron oxidation of the bis-anilido titanium(III) complex (Nacnac)Ti(NHAr)$_2$ (Nacnac$^-$ = ArNC(CH$_3$)CHC(CH$_3$)NAr, Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$) with AgOTf affords the cation [(Nacnac)Ti(NHAr)$_2$][OTf] which is isolated and shown to gradually transform, by α-hydrogen abstraction, to the terminal and four-coordinate titanium imide (Nacnac)Ti=NAr(OTf).

Low-coordinate transition metal imido complexes have experienced a remarkable growth in the last 30 years and constitute a landmark in inorganic chemistry.[1] Wolczanski[2] and Bergman[3] have prepared perhaps the most reactive imido complexes of the early-transition metals. This inherent reactivity can lead to the activation of relatively inert bonds such as primary and secondary[2,3] C–H bonds in alkanes and can be tailored to the unsaturated or electrophilic nature of the metal center. Parallel to the reactivity of early-transition metal imido systems, electron-rich late-transition metal imido complexes can also engage in C–H activation processes,[4] hence research in this area continues to draw great attention. Our recent report of the synthesis of a four-coordinate titanium alkylidene complex[5] and tertiary C–H bond activation reactions stemming from this complex[6] stimulated the pursuit of an analogous titanium imide complex. Inspired by the work of Wolczanski we attempted to prepare low-coordinate titanium imido complexes by an oxidatively induced α-abstraction reaction. Herein we report the conversion of a Ti(III) bis-anilido complex (Nacnac)Ti(NHAr)$_2$, (Nacnac$^-$ = ArNC(CH$_3$)CHC(CH$_3$)NAr, Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$),[7] to the corresponding cation [(Nacnac)-Ti(NHAr)$_2$]$^+$ and subsequent α-hydrogen abstraction to form a stable and terminal four-coordinate titanium imide complex.

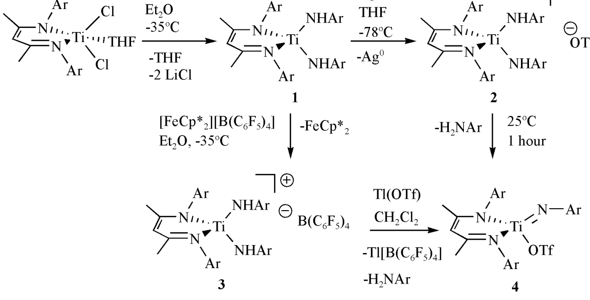
Our approach to preparing a low-coordinate and terminal titanium imido complex involved a similar strategy for the synthesis of the analogous alkylidene complex (Nacnac)-Ti=CH^{t}Bu(OTf) (Scheme 1).[5] Using Budzelaar's dichloride precursor (Nacnac)TiCl$_2$(THF)[5,8] and 2 equiv of LiNHAr we prepared the bis-anilido titanium(III) complex (Nacnac)Ti(N-HAr)$_2$ (**1**) in 92% yield as dark green blocks (Scheme 2).† In the absence of moisture and oxygen complex **1** is indefinitely stable in the solid state or in solution. X-band solution EPR spectra and magnetic measurements of **1** are consistent with a d^1 paramagnetic species.† The molecular structure of **1**† displays a four-coordinate Ti(III) complex in a tetrahedral environment. Salient features for the structure of **1** include titanium anilido distances of Ti(1)–N(34), 1.961(2) Å and Ti(1)–N(47), 1.966(2) Å.



Scheme 1 Synthesis of a four-coordinate titanium alkylidene *via* an oxidatively induced α-hydrogen abstraction reaction.

A cyclic voltammogram of a solution of **1** (THF–TBAH) indicated a *reversible* oxidation wave at −0.89 V (referenced *vs.* FeCp$_2$/FeCp$_2^+$) for the Ti(III)/Ti(IV) couple.† Chemically, it was determined that treatment of a thawing THF solution of **1** with AgOTf caused a color change from green to orange–red concomitant with formation of a Ag^0 mirror. Immediate workup after 5 minutes led to isolation of the bis-anilido triflato salt [(Nacnac)Ti(NHAr)$_2$][OTf] (**2**) as dark-red crystals in 71% yield (Scheme 2).† Complex **2** decomposes gradually in solution, and the yield of this complex is highly dependent on both time and temperature. Complex **2** was characterized by ^{1}H, ^{19}F, ^{13}C and IR spectroscopies.† Diagnostic features for **2** include two NH resonances centered at 11.1 and 10.4 ppm and one methyl environment for the β-carbon of the Nacnac backbone consistent with the molecule retaining C_s symmetry in solution. Complex **2** is insoluble and stable in most common organic solvents such as hexane, C$_6$H$_6$ and Et$_2$O, but soluble in THF and CH$_2$Cl$_2$ upon which it converts to a new complex and free aniline (*vide infra*). The insolubility of **2** in organic solvents suggests this complex to be a discrete salt where the OTf anion interacts weakly with the metal center.

Realizing the importance of the triflato anion in the stability of **2** we prepared a more stable salt of **2** using the weakly coordinating B(C$_6$F$_5$)$_4$ anion. Accordingly, oxidation of **1** with [FeCp*$_2$][B(C$_6$F$_5$)$_4$][9] in Et$_2$O at −35 °C affords in 92% isolated yield the bis-anilido salt [(Nacnac)Ti(NHAr)$_2$][B(C$_6$F$_5$)$_4$] (**3**) as brick-red microcrystals (Scheme 2).† Complex **3** shows nearly identical spectroscopic features to **2** in solution (δ for NH protons are 11.4 and 10.9 in the ^{1}H NMR spectrum of **3**).† The molecular structure of **3** was determined by single crystal X-ray diffraction studies and exhibits a four-coordinate titanium cation confined in a tetrahedral environment (Fig. 1).‡ Important crystallographic features for **3** include short Ti–N$_{\text{anilido}}$ bonds lengths of Ti(1)–N(33), 1.863(2) Å and Ti(1)–N(46), 1.875(2) Å, which is consistent with metal–ligand multiple bond character.[1] Most notably, the Ti–N$_{\text{anilido}}$ bond length is considerably shorter when compared to the neutral and d^1 complex **1** (*vide supra*). Other important crystallographic features for **3** include significantly different Ti(1)–N(33)–C(34) and Ti(1)–N(46)–C(47) angles of 132.8(9)° and 157.5(9)°, respectively. The α-hydrogens on the anilido nitrogens were located in the E-map and are indicative of agostic interactions with the Ti(IV) center.†



Scheme 2 Synthesis of complexes **1–4** starting from Budzelaar's precursor (Nacnac)TiCl$_2$(THF).

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† Electronic supplementary information (ESI) available: complete experimental, spectroscopic, analytical, and crystallographic details for complexes **1–4**. See http://www.rsc.org/suppdata/cc/b3/b304633h/

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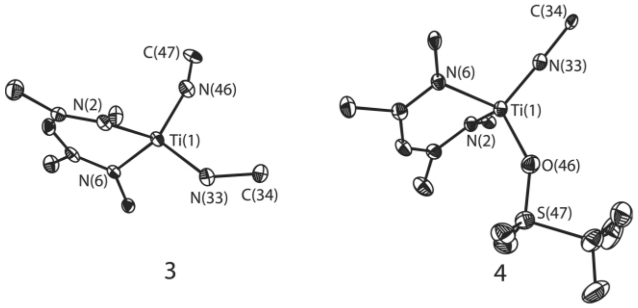

Fig. 1 Molecular structure of **3** (cation only) and **4** showing atom-labeling scheme with thermal ellipsoids at the 50% probability level. H-atoms and aryl groups with the exception of *ipso*-carbons on the nitrogen atoms the have been omitted for clarity.§

Intrigued by the instability of **2** we reasoned that decomposition of this complex lead to α-hydrogen abstraction concomitant with formation of a strong Ti=N bond and free aniline. In fact, if the reaction of **1** with AgOTf is allowed to proceed for 1 hour or longer, subsequent work-up of the mixture affords the titanium imido complex (Nacnac)Ti=NAr(OTf) (**4**) as red prisms in 67% yield (Scheme 2).† Hence, complex **2** is an intermediate to **4** inasmuch as stirring solutions of isolated **2** at room temperature in CH_2Cl_2 afford **4** and free aniline in quantitative yield.† The role of the anion is important in the stability of the cation since treatment of **3** with Tl(OTf)[10] in CH_2Cl_2 also promotes α-hydrogen abstraction to give **4** as evidenced by the ^1H NMR spectrum of the reaction mixture (Scheme 2).† The choice of solvent also plays an important role in the α-abstraction process since THF appears to accelerate the formation of **4**, relative to CH_2Cl_2. Single crystals of **4** were grown from pentane at -35 °C and the molecular structure is depicted in Fig. 1.¶ The structure of complex **4** shows a rare example of a four-coordinate titanium imido[2,5] complex with a short Ti(1)–N(33) bond length of 1.705(5) Å and a nearly linear $Ti–N_{imido}–C_{ipso}$ linkage (170.5(1)°). ^1H and ^{13}C NMR spectra are in accordance with **4** retaining C_s symmetry in solution, which is also consistent with the molecular structure. Complex **4** is isostructural to the reported alkylidene derivative (Nacnac)Ti=CH^{t}Bu(OTf).[6]

Our results suggest that both an electron deficient metal center in addition to coordination of a fifth ligand ($^-$OTf) promotes α-hydrogen abstraction. Coordination of $^-$OTf likely induces α-hydrogen abstraction by steric crowding of the anilido ligands. Alternatively, Lewis bases such as THF appear to enhance hydrogen abstraction, likely participating as proton carriers. Schrock and co-workers have observed closely related α-hydrogen abstraction reactions stemming from 5-coordinate d^0 molybdenum species.[11] In contrast to alkyl groups on titanium,[5] the anilido lone pair of electrons greatly increases the lifetime of the intermediate. This allows us to acquire a snapshot of long-lived intermediates associated with the oxidatively induced α-hydrogen abstraction process. The present work defines the steps by which one electron oxidation can lead to α-hydrogen abstraction and formation of a low-coordinate titanium-imido complex.

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Notes and references

‡ *Crystal data for* **3**·*Et₂O*, $C_{81}H_{87}BF_{20}N_4OTi$: Monoclinic, $P2_1/c$, a = 13.8639(6), b = 36.266(6), c = 13.9675(6) Å, β = 93.2700(10)°, Z = 4, μ(Mo-Kα) = 0.210 mm^{-1}, V = 7591.3(6) Å^3, D_c = 1.375 mg mm^{-3}, GoF on F^2 = 0.962, *R(F)* = 4.43% and *R(wF)* = 11.16%. Out of a total of 111677 reflections collected 17467 were independent and 9392 were observed (R_{int} = 10.95 %) with $I > 2\sigma I$ (orange prism, 0.25 × 0.25 × 0.07 mm, 27.55° ≥ Θ ≥ 2.07°).

§ CCDC 209461–209463. See http://www.rsc.org/suppdata/cc/b3/b304633h/ for crystallographic data in .cif or other electronic format.

¶ *Crystal data for* **4**·pentane, $C_{47}H_{70}F_3N_3O_3STi$: Triclinic, $P\bar{1}$, a = 10.271(4), b = 12.965(7), c = 18.451(3) Å, α = 93.783(7)°, β = 106.097(9)°, γ = 96.880°, Z = 2, μ(Mo-Kα) = 0.282 mm^{-1}, V = 2330.9(6) Å^3, D_c = 1.228 mg mm^{-3}, GoF on F^2 = 0.933, *R(F)* = 4.00% and *R(wF)* = 9.78%. Out of a total of 51577 reflections collected 10763 were independent and 7221 were observed (R_{int} = 8.34 %) with $I > 2\sigma I$ (orange prism, 0.30 × 0.25 × 0.25 mm, 27.60° ≥ Θ ≥ 2.07°). The crystal data shows a pseudo-inversion center and was merohedrally twinned (domain ratio 57 : 43).

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