Latent low-coordinate titanium imides supported by a sterically encumbering β-diketiminate ligand†

Falguni Basuli, Rodney L. Clark, Brad C. Bailey, Doug Brown, John C. Huffman and Daniel J. Mindiola*

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Addition of an equal molar quantity of R^- ($R = Me, SiMe_3$) to complex (Nacnac)Ti=NAr(OTf) ($Nacnac^- = [ArNC(tBu)]_2CH$, $Ar = 2,6\text{-}iPr_2C_6H_3$) forms the imido alkyl (Nacnac)Ti=NAr(R), which can be readily protonated to afford $[(Nacnac)Ti{=}NAr(L)]^+$ ($L = THF, Et_2O, \eta^1\text{-}C_6H_5NMe_2$), or treated with $B(C_6F_5)_3$ to afford the zwitterion (Nacnac)Ti=NAr(μ-CH_3)$B(C_6F_5)_3$.

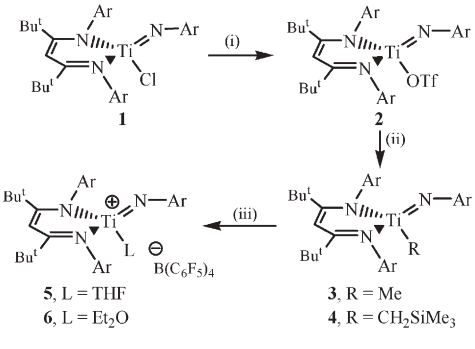
Transition metal complexes containing the imide $[NR]^{2-}$ functionality constitute a landmark in inorganic chemistry and such a ligand plays key roles in important processes such as group transfer (*e.g.*, aziridination, hydroamination),[1] intermolecular C–H activation,[2] and other catalytic reactions.[1,3,4] One of the versatile properties of the imide functionality is that it can not only become involved during the transformation, but on occasion it can be an ancillary ligand purely invoked in stabilizing reactive metal fragments throughout the catalytic cycle. One clear illustration of the latter class is Schrock's olefin metathesis catalyst $Mo(NAr)(CHR)(OCCH_3(CF_3)_2)$ ($Ar = 2,6\text{-}iPrC_6H_3$, $R = C(CH_3)_2Ph$), a complex which fails to display reactivity at the Mo=N linkage.[3] We specifically focus our attention on group 4 metal imides, since such a category of complexes has been demonstrated to possess rich chemistry.[2,5] One could conjecture that the hunt for reactive group 4 imides is most desirable for metal systems having unsaturated environments since organotransition metal complexes with low coordination numbers are inherently reactive and provide useful templates to study fundamental processes such as small molecule activation and catalysis.

The present study establishes that cationic and low-coordinate titanium imide complexes can be readily assembled *via* protonation of the imide alkyl (Nacnac)Ti=NAr(Me) ($Nacnac^- = [ArNC(tBu)]_2CH$, $Ar = 2,6\text{-}iPrC_6H_3$) with $[HNMe_2Ph][B(C_6F_5)_4]$ or by addition of $B(C_6F_5)_3$ to form the corresponding zwitterion. This new class of salts has been fully characterized including single crystal X-ray diffraction analysis.

In order to incorporate the terminal imide functionality on titanium a toluene solution of Li(Nacnac) with $TiCl_3(THF)_3$ was refluxed for 3 days. Upon work up, the four-coordinate imide (Nacnac)Ti=NAr(Cl) (**1**)† was isolated as orange crystals in 39% yield. It has been postulated in the literature that similar reductive C=N bond cleavage reactions using sterically demanding β-diketiminates occur through a putative $(Nacnac)_2TiCl$ intermediate, but the organic by-products generated from this type of reaction have not been identified.[6] Not surprisingly,[5] complex **1** is remarkably stable and fails to react with $Li[B(C_6F_5)_4]$ or LiR ($R^- = CH_3, CH_2SiMe_3$) even under forcing conditions.† The sterically imposing β-diketiminate in complex **1** is far more resistant to intramolecular transformations often encountered with the more common $[ArNC(CH_3)]_2CH$ ligand, which undergoes ligand deprotonation at the β–C methyl position.[7,8]

To promote salt metathesis in **1**, we incorporated a more efficient leaving group. Accordingly, treatment of **1** with AgOTf afford in excellent yield (76%), dark orange blocks of the triflatoimide (Nacnac)Ti=NAr(OTf) (**2**) (Scheme 1). Complex **2** was characterized by ^1H, ^{19}F, and ^{13}C spectroscopy† and data are consistent with the molecule retaining C_s symmetry in solution. The structure of complex **2**† shows a four-coordinate titanium imido[2,4,6,9] complex with a short Ti(1)–N_{imide} bond length of 1.708(5) Å and linear Ti–N_{imido}–C_{ipso} linkage (176.0(4)°, Fig. 1).† Unlike **1**,† the molecular structure of **2** reveals close Ti–C_β interactions with the NCCCN ring.† The AgOTf step is needed in order to promote reactivity of the titanium imide with lithium alkyl reagents. Consequently, treatment of **2** with ClMgR or LiR afford the imide alkyl complexes (Nacnac)Ti=NAr(R) in good yields (R = Me (**3**), 88%; $R = CH_2SiMe_3$ (**4**), 86%) as red blocks (Scheme 1).† It is imperative that the alkylation reaction be monitored *via* ^{19}F NMR spectra in order to ensure completion and prevent the thermal degradation of products **3** and **4**. ^1H NMR spectra are in accord with the molecules retaining C_s symmetry in solution and the alkyl resonances for both **3** and **4** are unambiguously located in ^1H NMR spectra (0.93 ppm, Ti*Me*; 1.31 and 0.34 ppm, $TiCH_2SiMe_3$).

Single crystal X-ray analysis also confirms the composition of compound **3**.† The molecular structure of **3** is displayed in Fig. 1 and reveals a four-coordinate titanium imide complex having a short Ti(1)–N_{imide} bond length of 1.726(1) Å and linear Ti–N_{imido}–C_{ipso} angle (172.4(1)). Due to the inherently electron deficient nature of **3**, the structure also reveals close proximity of the Ti to the β–C in the NCCCN ring (2.672(3) Å).[10] Given the electron deficient count in **3** and **4**, it is rather remarkable that both NMR spectra and X-ray lack evidence for α-H agostic interactions taking place.



Scheme 1 Synthesis of compounds **1–4** and the cations of **5** and **6**. *Conditions*: (i) 1 equiv. of AgOTf, THF, −35 °C; (ii) 1 equiv. of LiR ($R = CH_3, CH_2SiMe_3$), −35 °C, Et_2O; (iii) 1 equiv. of $[HNMe_2Ph][B(C_6F_5)_4]$, 25 °C, few drops of THF or Et_2O, in C_6H_6 or C_6H_5F.

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† Electronic supplementary information (ESI) available: complete experimental, spectroscopic, analytical, and crystallographic details for complexes 1–3 and 5–7. See http://www.rsc.org/suppdata/cc/b5/b500350d/
*Mindiola@indiana.edu

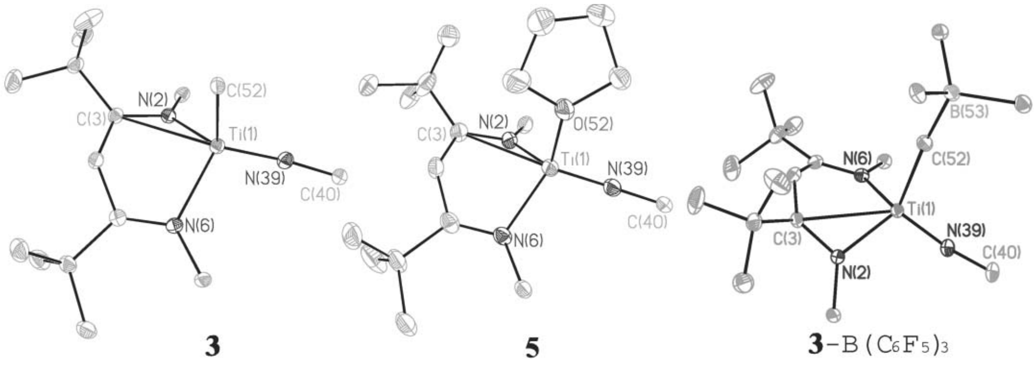


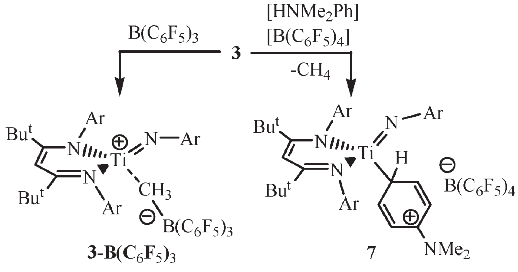
Fig. 1 Molecular structures of **3**, the cation component of **5**, and the zwitterion **3-B(C_6F_5)$_3$** with thermal ellipsoids at the 50% probability level. All H-atoms, solvent molecules, and aryl groups with the exception of the *ipso*-carbons have been omitted for clarity. The structure of **3** contains two independent molecules. Selected metrical parameters (Å, °) for **3**: Ti(1)–C(52), 2.170(4); Ti(1)–N(39), 1.726(1); Ti(1)–N(2), 1.998(1); Ti(1)–N(6), 2.089(1); Ti(1)–C(3), 2.672(3); N(2)–Ti(1)–N(6), 99.34(4); Ti(1)–N(39)–C(40), 172.4(1). For **3-B(C_6F_5)$_3$**: Ti(1)–C(52), 2.412(1); B(53)–C(52), 1.680(6); Ti(1)–N(39), 1.7186(9); Ti(1)–N(2), 1.9656(9); Ti(1)–N(6), 2.0817(9); Ti(1)–C(3), 2.6342(10); N(2)–Ti(1)–N(6), 99.10(4); Ti(1)–N(39)–C(40), 171.86(8); Ti(1)–C(52)–B(53), 175.28(7). For **5**: Ti(1)–O(52), 2.042(4); Ti(1)–N(39), 1.709(6); Ti(1)–N(2), 1.951(6); Ti(1)–N(6), 2.061(5); Ti(1)–C(31), 2.662(9); N(2)–Ti(1)–N(6), 100.10(6); Ti(1)–N(39)–C(40), 173.3(4).

Addition of [$HNMe_2Ph$][$B(C_6F_5)_4$] to **3** in C_6H_6/L rapidly generates CH_4 concomitant with formation of cationic and four-coordinate titanium imide[11] [(Nacnac)Ti=NAr(L)][$B(C_6F_5)_4$] (L = THF, **5**; L= Et_2O, **6**) as orange-red needles in 76–82% isolated yield (Scheme 1).† Complexes **5** and **6** are exceedingly reactive, which is manifested by their rapid decomposition in halogenated solvents. For instance, solutions of **5** or **6** rapidly abstract Cl when exposed to CH_2Cl_2 or $CHCl_3$ to afford **1** quantitatively. Attempts to generate the solvent-free cation [(Nacnac)Ti=NAr][$B(C_6F_5)_4$] are fraught with formation of the adducts **5** and **6** *via* minimal traces of coordinating solvents in the glovebox atmosphere. Complex **5** and **6** are persistently stable in solvents such as C_6H_5F or C_6H_6.

Single crystals of **5**‡ and **6**† were grown at room temperature, and the molecular representation for **5** is depicted in Fig. 1. The structure of **5** portrays a cationic and low-coordinate titanium(IV) complex bearing a terminal imide functionality and short Ti=N bond (Ti=N, 1.709(6) Å; Ti=N–C, 173.3(4)).[1] The molecular structure of the Et_2O adduct **6** also displays similar metrical parameters to **5** but suffers from partial occupancy of THF and Et_2O.† As observed with the neutral titanium imide species, the imide aryl group in **5** is along the σ-plane bisecting N–Ti–N and disposed *syn* with respect to the THF ligand (Fig. 1).† The flanking aryl groups and sterically imposing *t*Bu substituents in the β-carbon position consequently push the Ti atom considerably out of the NCCCN plane (~0.93 Å) and as a result there is a close interaction between the Ti center and the β–C within the NCCCN ring (Ti(1)–C(3), 2.662(9) Å).

To avoid Lewis base coordination in **5** and **6**, complex **3** was treated with 1 equiv. of $B(C_6F_5)_3$ in C_6H_5F to afford the zwitterion (Nacnac)Ti=NAr(μ–Me)$B(C_6F_5)_3$ (**3-B(C_6F_5)$_3$**) quantitatively (Scheme 1). Solids and solvents must be free of coordinating solvents to avoid adducts such as **5** and **6** from forming. The ^{11}B NMR spectrum (−13.5 ppm) is consistent with a zwitterion system resulting from methide abstraction. In addition, the single crystal X-ray diffraction analysis of **3-B(C_6F_5)$_3$**§ supports a five-coordinate carbon, which results in significant elongation of the Ti–CH_3 distance (2.412(1) Å, Fig. 1). The perfluorinated aryls on the boron are twisted in a propeller like fashion and deviation of the B atom from the *ipso*-C_3 plane (~0.58 Å) further reveal Lewis acid adduct formation in **3-B(C_6F_5)$_3$**. With the exception of the $CH_3B(C_6F_5)_3$ ligand in **3-B(C_6F_5)$_3$**, all other structural parameters are very similar to the (Nacnac)Ti=NAr scaffold in **3**.

Protonation of **3** with [$HNMe_2Ph$][$B(C_6F_5)_4$] in C_6H_5F leads instead to the *p*-dimethylaminoarene adduct [(Nacnac)Ti=NAr(η^1-$C_6H_5NMe_2$)][$B(C_6F_5)_4$] (**7**) in 70% isolated yield (Scheme 2). The connectivity in **7** was inferred by a combination of ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra in addition to single crystal X-ray diffraction data (Fig. 2).¶ Most impressively, coordination of the amine (NMe_2Ph) does not occur at the nitrogen position, but instead the electrophilic metal center activates the *p*-C position on the aryl group (Ti(1)–C(52), 2.337(5) Å). This distance is long when compared to Ti–Ph ligands, but reasonable to Ti–C lengths for delocalized ligands such as $C_6H_6^-$ and $C_5H_5^-$, and shorter than the Ti–CH_3 length in **3-B(C_6F_5)$_3$** (*vide supra*). Evidence for the *ipso*-C being activated is provided by the dimethylamino group in the structure of **7**, which is planar and orientated along the aryl group (Fig. 2). However, the aryl C–C distances of the NMe_2Ph ligand do not support a localized charge in complex **7**.[12] ^1H and ^{13}C NMR spectra of **7** in C_6D_5F are consistent with C_s symmetry in solution and the *p*-H and carbon resonances for the bound dimethylaniline were unambiguously assigned at 6.87 and 119 ppm, respectively, *via* a combination of HMQC, and ^{13}C NMR (^1H coupled and decoupled) experiments.† The NMe_2Ph chemical shifts are virtually indistinguishable from those reported for the free dimethylaniline and addition of excess NMe_2Ph does not display two sets of resonances suggesting that the coordinating aniline in **7** might be undergoing rapid exchange with C_6D_5F/NMe_2Ph on the NMR time scale.† Hence, complex **7** can be best described as an arenium species[13] or Meisenheimer-type



Scheme 2 Synthesis of compounds **3-B(C_6F_5)$_3$** and **7**.

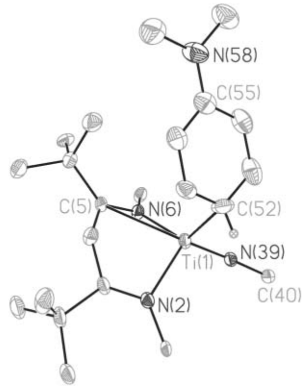


Fig. 2 Molecular structure of the cation component of **7** with thermal ellipsoids at the 50% probability level. All H-atoms (except for C52) and aryl groups with the exception of the *ipso*-carbons on N2, N6, and N39 have been omitted for clarity. Selected metrical parameters (Å, °) for **7**: Ti(1)–C(52), 2.337(5); Ti(1)–N(39), 1.719(3); Ti(1)–N(2), 2.060(3); Ti(1)–N(6), 1.984(3); Ti(1)–C(5), 2.642(4); C(55)–N(58), 1.358(5); Ti(1)–H, 2.31(4); N(2)–Ti(1)–N(6), 99.5(2); Ti(1)–N(39)–C(40), 174.3(3).

complex resulting from arene coordination to a highly electrophilic metal fragment [(Nacnac)Ti=NAr]$^+$. Interestingly, the coordination of the arene in complex **7** is in stark contrast to reported η^6-arene complexes such as $[([ArNC(CH_3)]_2CH)Sc(Me)(\eta^6\text{-arene})]^+$.[14] Such an unusual coordination mode can be correlated to sterics or the electronically rich nature of the arene motif. As expected, complex **7** reacts readily with THF and Et_2O to afford adducts **5** and **6** respectively, along with free NMe_2Ph.

In summary, we have shown that the sterically demanding Nacnac$^-$ ligand can stabilize low-coordinate complexes possessing terminal Ti=N linkages. In all these electron deficient systems it appears that interaction with the β-C center is key in order for the [(Nacnac)Ti=NAr]$^+$ fragment to gain additional electron density from the C–N bond. We are currently exploring the reactivity of this new family of titanium imides.

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Falguni Basuli, Rodney L. Clark, Brad C. Bailey, Doug Brown, John C. Huffman and Daniel J. Mindiola*
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana, 47405, USA.
E-mail: Mindiola@indiana.edu; Fax: +1-812-855-8300;
Tel: +1-812-855-2399

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‡ *Crystal data for* **5**, $C_{79}H_{86}BF_{20}N_3O_2Ti$: Triclinic, $P\bar{1}$, a = 13.505(1), b = 15.087(2), c = 18.955(4) Å, α = 99.273(2), β = 104.999(2), γ = 93.197(2)°, Z = 2 μ(Mo–Kα) = 0.217 mm^{-1}, V = 3662.6(5) Å^3, D_c = 1.404 mg mm^{-3}, GoF on F^2 = 0.833, R_1 = 4.25% and wR_2 = 9.34% (F^2, all data). Reflections; collected/unique/observed 59016/16905/9698 (R_{int} = 7.68%) ($I > 2\sigma I$) (red-pink prism, 0.28 × 0.18 × 0.15 mm, 27.55° $\geqslant \Theta \geqslant$ 1.98°).

§ *Crystal data for* ***3-B(C₆F₅)₃***, $C_{72}H_{78}BF_{16}N_3Ti$: Triclinic, $P\bar{1}$, a = 13.372(4), b = 14.027(4), c = 17.625(8) Å, α = 79.495(3), β = 88.114(3), γ = 86.204(3)°, Z = 2 μ(Mo–Kα) = 0.224 mm^{-1}, V = 3242.5(6) Å^3, D_c = 1.381 mg mm^{-3}, GoF on F^2 = 0.905, R_1 =3.84% and wR_2 = 9.41% (F^2, all data). Reflections; collected/unique/observed 109449/24759/16524 (R_{int} = 6.25%) ($I > 2\sigma I$) (red-pink prism, 0.28 × 0.25 × 0.25 mm, 33.16° $\geqslant \Theta \geqslant$ 2.05°).

¶ *Crystal data for* **7**, $C_{79}H_{81}BF_{20}N_4Ti$: Triclinic, $P\bar{1}$, a = 12.645(7), b = 17.067(2), c = 17.378(2) Å, α = 94.190(4)°, β = 106.094(4), γ = 93.621(4), Z = 2, μ(Mo–Kα) = 0.220 mm^{-1}, V = 3580.0(8) Å^3, D_c = 1.415 mg mm^{-3}, GoF on F^2 = 0.874, $R(F)$ = 5.77% and R(wF) = 12.93%. Reflections; collected/independent/observed 22136/16157/6812 (R_{int} = 6.53%) ($I > 2\sigma I$) (orange prism, 0.25 × 0.25 × 0.20 mm, 27.54° $\geqslant \Theta \geqslant$ 2.13°). CCDC 260834–260840. See http://www.rsc.org/suppdata/cc/b5/b500350d/ for crystallographic data in CIF or other electronic format.

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