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Reductive C–N bond cleavage of the NCCCN β-diketiminate backbone: A direct approach to azabutadienyl and alkylidene-anilide scaffolds

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Abstract

Tetrahydrofuran/toluene solutions of (nacnac)TiCl$_2$ (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) react readily with KC$_8$ to afford the titanium imide (ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(THF)Cl (**1**) in 67% isolated yield. Complex **1** forms from the two-electron reductive C–N bond cleavage of the β-diketiminate ligand. Likewise, reduction of (nacnac)TiCl(NHAr) (**2**), prepared in 85% yield from (nacnac)TiCl$_2$ and LiNHAr, with KC$_8$ results in formation of the imide-anilide analogue (ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(NHAr) (**3**) in 88% yield. Another reductant such as Li^{t}Bu (3 equiv.) reacts cleanly with the precursor (nacnac)TiCl$_2$ to afford the alkylidene-ate complex [Li(Et$_2$O)][(ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(Et$_2$O)] (**4**), in 81% yield. Complexes **1**–**4** have been characterized by ^{1}H and ^{13}C NMR spectra as well as single-crystal X-ray diffraction analysis. Plausible mechanisms to formation of compounds **1**, **3** and **4** are also presented and discussed.

Keywords: Crystal structures; Titanium complex; Imine functionality; Imide complexes; Alkylidene

1. Introduction

The β-diketiminate ancillary framework has played a pivotal role in the assembly of reactive complexes in essentially all groups of the periodic table [1]. In particular, this ligand system has allowed the creation of organotransition catalysts, [1–9] the modeling of biologically relevant active sites, [1,10,11] the assembly of terminal and reactive multiply bonded metal–ligand functionalities such as alkylidenes, [12,13] alkylidynes, [14] imides, [15–18] and phosphinidenes, [19] the intermolecular activation of inert substrates such as alkanes [20,21] and N$_2$, [21–23] as well as generation of low valent complexes bearing exotic oxidation states [1,24–28].

Apart from the ubiquitous β-diketiminate system being a monoanionic spectator ligand, several studies by us and others have now demonstrated that such a scaffold possesses the ability to undergo various types of transformations such as deprotonation reactions, [1,12c,29] intra- [2a,12b,12c,12e,30] and intermolecular [1,20,21] C–H activation reactions, electrophilic activation of the NCCCN γ-C carbon, [1,29,30] cross-metathesis reactions involving the imine functionality of the ligand, [12,14,19a] and more recently, C–N bond cleavage reactions of the NCCCN ligand backbone [17,23,31,32]. The latter transformation has not only been observed for Zr(IV) [31,32] and Hf(IV) [32] reduction reactions, but also via the one- and two-electron reductions of Ti(III) [23] and Ti(IV) [32] complexes, respectively. Most notably, this type of transformation is particularly attractive since the NCCCN ring of the β-diketiminate scaffold results in formation of a metal imide concomitant with an azabutadienyl ancillary template.

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In this work, we report that one-electron reduction reactions of Ti(III) precursors containing the sterically demanding β-diketiminate ligand nacnac$^-$ (nacnac= [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), leads to cleavage of the backbone C–N bond to form terminal titanium imides supported by the azabutadienyl framework [ArN(^{t}Bu)CCHC(^{t}Bu)]$^-$. Our results compliment previous studies by Stephan [23] and Tokitoh [32] involving formation of a ring-contracted azabutabutadienyl ligand from reduction of the β-diketiminate C–N bond. In addition, we have also discovered that the Ti(III) β-diketiminate precursor (nacnac)TiCl$_2$, when reduced by three-electrons, can generate the alkylidene-ate complex [Li(Et$_2$O)][(ArN(^{t}Bu)-CCHC(^{t}Bu))Ti=NAr(Et$_2$O)].

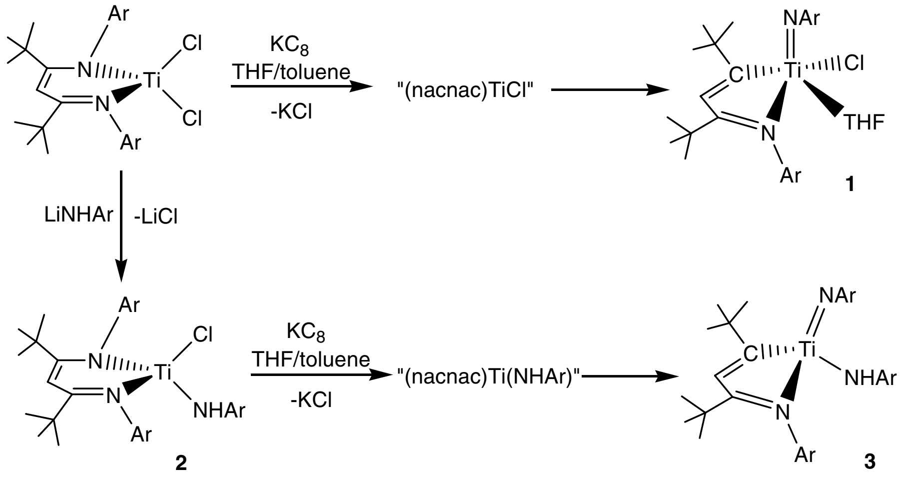
2. Results and discussion

2.1. Reduction of (nacnac)TiCl$_2$ and (nacnac)TiCl(NHAr), and formation of the monoanionic azabutadienyl framework

One-electron reduction of (nacnac)TiCl$_2$ [12b] (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with KC$_8$ [33] in cold THF/toluene effects C–N bond cleavage to afford the titanium azabutadienyl-imide complex (ArN(^{t}Bu)-CCHC(^{t}Bu))Ti=NAr(THF)Cl (**1**) in 67% isolated yield (Scheme 1). Complex **1** can be best described as a titanium imide supported by a monoanionic η^2-vinyl-imine ligand. Stephan and co-workers proposed compounds similar to **1** as likely intermediates in their reduction studies of Ti(III) precursors invoking the less hindered β-diketiminate ligand [ArNC(Me)]$_2$CH (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) [23]. Likewise, Tokitoh and co-workers have reported both the two and one electron reduction reactions stemming from Ti(IV) and Ti(III) precursors, respectively, containing an unsymmetrically substituted β-diketiminate ligand MesNC(Me)CHC-(Me)N(Tbt), where Tbt = 2,4,6-{(Me$_3$Si)$_2$CH}$_3$C$_6$H$_2$ and Mes = 2,4,6-Me$_3$C$_6$H$_2$ [32]. In Tokitoh's studies, the possibility of a Ti(II) intermediate being involved in these reactions was further corroborated by treatment of the lithium β-diketiminate salt with Gambarotta's Ti(II) precursor, TiCl$_2$(tmeda)$_2$, [34] to afford the same Ti(IV) product resulting from reductive C–N bond cleavage [32]. Likewise, Stephan's studies also suggested that a Ti(II) intermediate was involved in the C–N bond cleavage process, since treatment of the Ti(III) precursor ([ArNC(Me)]$_2$CH)TiCl$_2$ with Cp$^-$, followed by a one electron reduction, resulted in N$_2$ activation by two Ti(II) scaffolds [23].

For us, complex **1** exhibits remarkable stability as a solid or in solution, and has been characterized by ^{1}H and ^{13}C NMR spectroscopy in addition to elemental analysis. The ^{1}H NMR spectrum of **1** revealed three inequivalent isopropyl methine environments consistent with one of the N-aryl groups having restricted rotation. We propose that hindered rotation occurs at the azabutadienyl aryl group as opposed to the more unrestricted aryl imide. This features also results in the observation of six different isopropyl methyl resonances. However, the most notable sign of asymmetry resulting from cleavage of the ligand stems from the observation of two inequivalent ^{t}Bu groups centered at 1.56 and 1.04 ppm. In the ^{13}C NMR spectrum, the vinylic carbon resonance was located unambiguously at 258.9 ppm. Similar chemical shifts have been observed for the Ti(IV) derivative reported by Stephan [23] and Tokitoh, [32] as well as the Zr(IV) analogue (ArN(^{t}Bu)-CCHC(^{t}Bu))Zr=NAr(THF)Cl [31]. Hence, all of these spectroscopic features clearly renders complex **1** C_1 symmetric in solution.

As previously suggested by Stephan and Tokitoh, formation of **1** from the one-electron reduction of (nacnac)TiCl$_2$ likely involves generation of a putative Ti(II) intermediate "(nacnac)TiCl", which readily undergoes a two electron intramolecular transfer pathway to reduce the N–C bond (Scheme 1). We wondered whether substitution of one chloride ligand for a more hindered ligand might result in isolation of the elusive Ti(II) intermediate.



Scheme 1.

Stephan and co-workers applied this same strategy using a Cp^- ancillary set, which underwent N_2 activation under reducing conditions to form the N_2-bridging dimer $[([ArNC(Me)]_2CH)TiCp]_2(\mu\text{-}N_2)$ [23]. Accordingly, when (nacnac)$TiCl_2$ is treated with one equiv. of LiNHAr in toluene at −35 °C, complex (nacnac)Ti(NHAr)Cl (**2**) is formed in 85% yield subsequent to recrystallization from Et_2O (Scheme 1). Complex **2** is a green colored paramagnetic material, and consequently reveals an Evans solution magnetic measurement of 1.88 μ_B consistent with a monomeric d^1 species. Despite having a sterically encumbering anilide ligand, complex **2** also undergoes smooth C–N bond cleavage under reducing conditions (1 equiv. of KC_8, THF) to afford the anilide derivative of **1**, namely the complex $(ArN(^tBu)CCHC(^tBu))Ti{=}NAr(NHAr)$ (**3**) in 88% isolated yield (Scheme 1).

Complex **3** also manifests similar NMR spectroscopic features to **1**, consistent again with these systems having C_1 symmetry in solution. In addition to the two inequivalent ^tBu groups, complex **3** displays four different isopropyl methine resonances, which suggests that both the imide and anilide aryls are freely rotating in solution. In addition, the vinylic carbon resonance was located at 250.4 ppm in the ^{13}C NMR spectrum. Unlike **1**, substitution of the chloride for a more hindered ligand such as – NHAr results in a lower coordination number on Ti(IV) (no THF resonances were observed, which is not the case for compound **1**).

2.1.1. Molecular structure determination of complex 1

The molecular structure of **1** displays a monomeric, five coordinate Ti system supported by a monoanionic azabutadienyl, a terminal aryl-imido (Ti(1) = N(27), 1.712(9) Å; Ti=N–C_{ipso}, 172.2(7)°), a THF (Ti(1)–O(40), 2.205(6) Å), and a chloride ligand (Ti(1)–Cl(2), 2.3103(8) Å) occupying the fifth coordination site (Fig. 1). Crystallographic data for **1** are displayed in Table 1 and selected metrical parameters are shown in Table 2. As noted in Table 1, selected metrical parameters for the NCCC ring in **1** are consistent with a monoanionic η^2-vinyl-imine ligand with the most prominent feature being the Ti–C_{vinyl} distance of 2.171(2) Å. As observed with other anionic azabutadienyl frameworks, [23,31,32] the Ti atom virtually sits in the plane of the azabutadienyl NCCC ring (~0.06 Å).

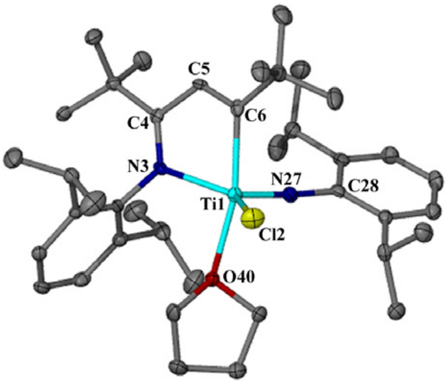


Fig. 1. Molecular structure of **1** displaying thermal ellipsoids at the 50% probability level with distances reported in (Å) and angles in (°). All H-atoms have been omitted for clarity. Crystallographic and refinement data are displayed in Table 1 and selected metrical parameters are displayed in Table 2.

2.1.2. Molecular structure determination of complex 2

Complex **2** crystallizes in the space group $P\bar{1}$ and the molecular structure exposes a four coordinate Ti(III) mono-anilide species supported by a sterically demanding β-diketiminate ligand. A perspective view of the molecular structure of **2** is depicted in Fig. 2 along with selected metrical parameters. Crystallographic and refinement data for **2** are shown in Table 1. In the molecular structure of **2**, the Ti atom sits ~0.29 Å above the mean plane defined by the NCCCN atoms of the β-diketiminate ring. The structure clearly shows that a chloride ligand has been replaced by a encumbering anilide ligand (Ti(1)–N(40), 1.938(2) Å). The solid state structure of **2** displays no other exceptional features.

2.1.3. Molecular structure determination of complex 3

The molecular structure of **3** clearly depicts a four-coordinate titanium imide scaffold supported by a monoanionic azabutadienyl and an anilide ligand (Fig. 3). The solid state structure of **3** closely resembles that of **1**, whereby a sterically hindered anilide has replaced both the chloride and THF ligands. Salient features for the structure of **3** include a linear angle (168.4(6)°) and terminal imide group (1.720(6) Å), as opposed to the anilide functionality which contains a longer Ti–N distance (Ti(1)–N(39), 1.959(6) Å) and bent linkage (Ti(1)–N(39)–C(40), 142.2(5)°). The Ti atom lies within the NCCC ring composing the monoanionic azabutadienyl ligand (~0.06 Å), while the Ti–C_{vinyl} distance (2.139(8) Å) is similar to that observed for the molecular structure of **1**. Crystallographic data for **3** are displayed in Table 1 and selected metrical parameters are shown in Table 2.

2.2. Reduction studies of (nacnac)$TiCl_2$ with Li^tBu, and formation of an ate complex bearing the alkylidene-anilide framework

Our group [35] has shown that Li^tBu can be often used as a soluble one-electron source. Accordingly, when complex (nacnac)$TiCl_2$ is treated with one equiv. of Li^tBu in Et_2O, the complex $[Li(Et_2O)][(ArN(^tBu)CCHC(^tBu))\text{-}Ti{=}NAr(Et_2O)]$ (**4**) is isolated in poor yields (10–20%). In addition to **4**, a significant amount of starting material, (nacnac)$TiCl_2$, was recovered from the mixture. Therefore, formation of **4** suggested that a four-electron redox process had occurred whereby the C=N linkage has been reduced to an alkylidene and imide functionality. This result is in stark contrast to formation of **1** from (nacnac)$TiCl_2$, and **3** from **2**, where a two-electron reduction process had occurred (one electron from Ti(III) and one from the

Table 1
Summary of crystallographic data and structure refinement for complexes **1**–**4**

Complex	**1**	**2** · 1/2C_6H_{14}	**3**	**4**
Formula	$C_{39}H_{61}ClN_2OTi$	$C_{50}H_{78}ClN_3Ti$	$C_{47}H_{71}N_3Ti$	$C_{43}H_{73}LiN_2O_2Ti$
FW	657.25	804.50	725.97	704.87
Space group	P2(1)/c	$P\bar{1}$	Pca2(1)	Pbcn
a (Å)	9.334(2)	10.841(2)	23.693(6)	35.344(3)
b (Å)	17.902(4)	12.761(4)	9.729(2)	11.6940(9)
c (Å)	22.644(5)	19.335(2)	18.762(5)	20.663(6)
α (°)	90.00	78.551(3)	90.00	90.00
β (°)	97.281(7)	74.627(3)	90.00	90.00
γ (°)	90.00	65.944(3)	90.00	90.00
V (Å^3)	3753.2(15)	2342.7(4)	4324.6(19)	8540.3(11)
Z	4	2	4	8
D_{calc}	1.163	1.140	1.115	1.096
Linear absorption coefficient	0.330	0.275	0.232	0.235
$F(0\,0\,0)$	1424	876	1584	3088
Crystal color/solvent	orange Et_2O	green hexane	brown Et_2O	orange Et_2O
Crystal form	spherical-like	spherical-like	plate	elongated prism
Crystal size (mm)	0.15 × 0.15 × 0.15	0.15 × 0.15 × 0.15	0.40 × 0.08 × 0.04	0.40 × 0.25 × 0.14
Θ range (lattice, °)	2.14–27.55	2.10–27.55	2.03–27.57	2.05–33.16
Index range	$-12 \leqslant h \leqslant 12$, $-23 \leqslant k \leqslant 23$, $-29 \leqslant l \leqslant 29$	$-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-25 \leqslant l \leqslant 25$	$-30 \leqslant h \leqslant 30$, $-12 \leqslant k \leqslant 12$, $-21 \leqslant l \leqslant 24$	$-50 \leqslant h \leqslant 54$, $-18 \leqslant k \leqslant 17$, $-31 \leqslant l \leqslant 29$
Reflections collected	71743	29534	31106	92491
Unique reflections $F > 4\sigma(F)$	8644	10797	8781	16280
Observed reflections	4027	6648	2874	7430
R_{int}	0.1803	0.0603	0.3075	0.1203
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0370$, $wR_2 = 0.0492$	$R_1 = 0.0538$, $wR_2 = 0.1306$	$R_1 = 0.0755$, $wR_2 = 0.1405$	$R_1 = 0.0443$, $wR_2 = 0.0754$
R indices (F^2, all data)	$R_1 = 0.1202$, $wR_2 = 0.0656$	$R_1 = 0.0881$, $wR_2 = 0.1450$	$R_1 = 0.2364$, $wR_2 = 0.1878$	$R_1 = 0.1179$, $wR_2 = 0.0907$
Goodness-of-fit on F^2	0.691	0.924	0.771	0.759

Table 2
Selected structural parameters for complexes **1**, **3** and **4**

Complex	**1**	**3**	**4**
Ti–C_α	Ti(1)–C(6), 2.171(2)	Ti(1)–C(5), 2.139(8)	Ti(1)–C(5), 1.965(4)
Ti–N_{imide}	Ti(1)–N(27), 1.712(9)	Ti(1)–N(26), 1.720(6)	Ti(1)–N(26), 1.798(2)
Ti–N	Ti(1)–N(3), 2.211(9)	Ti(1)–N(2), 2.153(6)	Ti(1)–N(2), 1.945(1)
Ti–Cl	Ti(1)–Cl(2), 2.3103(8)	n/a	n/a
Ti–O	Ti(1)–O(40), 2.205(6)	n/a	Ti(1)–O(39), 2.117(1)
C_α–C_β	C(6)–C(5), 1.342(3)	C(5)–C(4), 1.36(1)	C(5)–C(4), 1.447(9)
C_β–C_β	C(5)–C(4), 1.465(3)	C(4)–C(3), 1.44(1)	C(4)–C(3), 1.395(9)
C_β–N	C(4)–N(3), 1.307(3)	C(3)–N(2), 1.331(9)	C(3)–N(2), 1.414(7)
Ti–N_{imide}–C	Ti(1)–N(27)–C(28), 172.2(7)	Ti(1)–N(26)–C(27), 168.4(6)	Ti(1)–N(26)–C(27), 177.6(1)

Bond lengths are reported in (Å) and bond angles in (°). Only distances for carbon atoms of the NCCC framework are included.

reducing agent KC_8). Gratifyingly, when complex **1** was treated with three equiv. of Li^{t}Bu, formation of **4** was significantly improved to 81% yield (Scheme 2).

The NCCC framework in **4** can be referred to as a chelating alkylidene-anilide ligand. However, the anionic charge in **4** can also be delocalized about the alkylidene carbon, Ti, and imide nitrogen atoms as depicted in Scheme 2. Diagnostic spectroscopic features for **4** include the observation of the alkylidene carbon resonance at 210.5 ppm (^{13}C NMR). This chemical shift has dramatically shifted from further downfield vinyl carbon in compounds such as **1** and **3**, and is comparable to the few examples of titanium alkylidene-ate complexes (also referred to as a metallacyclic alkylidene) reported by Scholz and co-worker [36]. Both ^{1}H and ^{13}C NMR spectra are consistent with complex **4** having C_1 symmetry in solution. Despite us having spectroscopic evidence suggesting that **4** contains an alkylidene moiety, we resorted to single-crystal X-ray diffraction analysis to further corroborate our claims (vide infra).

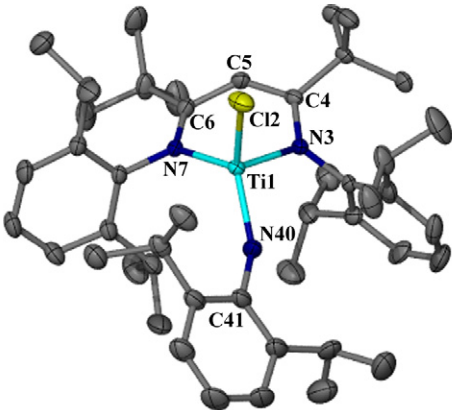


Fig. 2. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level with distances reported in (Å) and angles in (°). All H-atoms and a 1/2 hexane molecule have been omitted for clarity. Crystallographic and refinement data are displayed in Table 1. Ti(1)–N(40), 1.938(2); Ti(1)–N(3), 1.986(8); Ti(1)–N(7), 2.096(2); Ti(1)–Cl(2), 2.3028(7); N(7)–C(6), 1.320(3); C(6)–C(5), 1.440(3); C(5)–C(4), 1.370(3); C(4)–N(3), 1.378(3); N(7)–Ti(1)–N(3), 91.62(8); N(7)–Ti(1)–Cl(2), 114.05(6); N(7)–Ti(1)–N(40), 114.13(9); N(3)–Ti(1)–Cl(2), 105.08(6); N(3)–Ti(1)–N(40), 98.97(9); Cl(2)–Ti(1)–N(40), 124.75(8); Ti(1)–N(40)–C(41), 145.7(2).

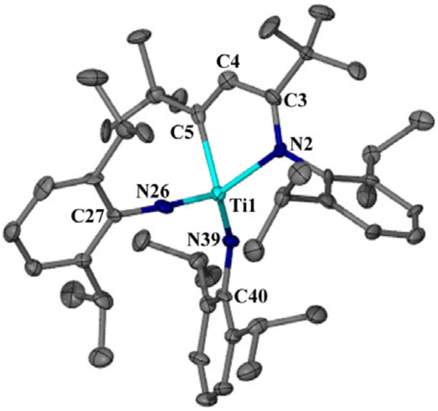


Fig. 3. Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level with distances reported in (Å) and angles in (°). All H-atoms have been omitted for clarity. Crystallographic and refinement data are displayed in Table 1 and selected metrical parameters are displayed in Table 2.

Based on previous studies by Stephan, [23] Tokitoh, [32] and us [31] we propose that complex **4** is likely generated via a multi-electron redox process as depicted in Scheme 2. The first step in formation of **4** possibly involves a one-electron reduction and transmetallation step of (nacnac)$TiCl_2$ to afford "(nacnac)Ti(^{t}Bu)". By virtue of an intramolecular two-electron process, putative "(nacnac) Ti(^{t}Bu)" is prone to C–N bond rupture to generate "(ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(^{t}Bu)". The latter intermediate can undergo nucleophilic attack by another Li^{t}Bu equiv. across the imine functionality to generate a hypothetical ate-species "[Li][(ArN(^{t}Bu)$_2$CCHC(^{t}Bu))Ti=NAr(^{t}Bu)]", which can then extrude two equiv. of ^{t}Bu radical to produce **4** (Scheme 2). However, given the complexity of this reaction, we are unsure of the order of events. For example, does C–N bond rupture occur prior to transmetallation by a second Li^{t}Bu equiv.? To test this hypothesis, we treated complex **1** with 2 equiv. of Li^{t}Bu in toluene/Et_2O and found that complex **4** was not one of the several products generated in the reaction mixture. In addition, one can also speculate that intermediate "(ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(^{t}Bu)" can undergo ^{t}Bu radical loss to form a Ti(III) species, prior to nucleophilic attack by Li^{t}Bu (Scheme 2). Regardless of what steps might be involved in such an interesting process we are confident that each Li^{t}Bu molecule is behaving as a one-electron reductant, and that formation of **4** from (nacnac)$TiCl_2$ involves an overall four-electron redox process (three electrons from Li^{t}Bu and one from Ti(III) precursor (nacnac)$TiCl_2$).

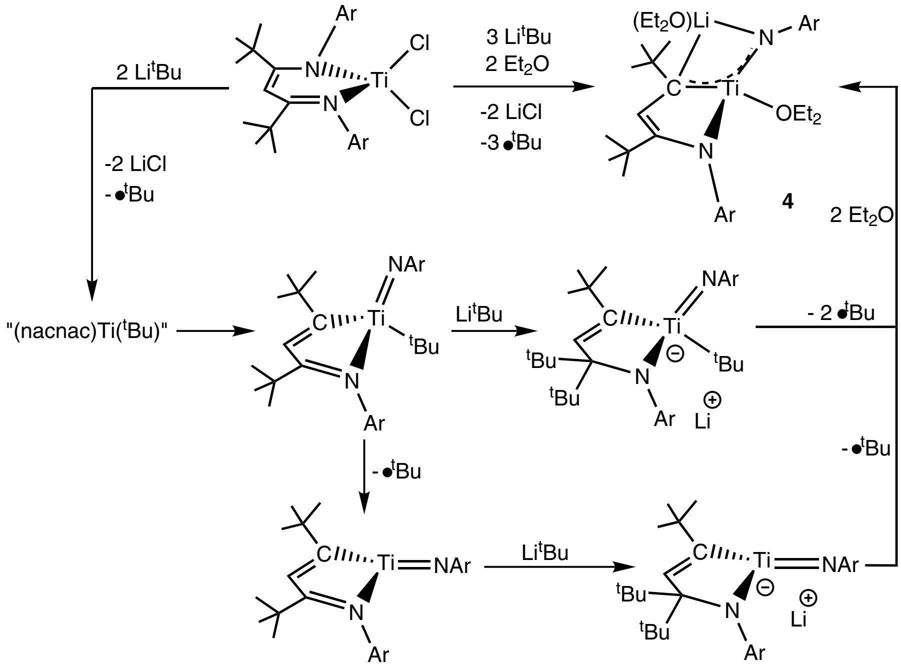
2.2.1. *Molecular structure determination of complex 4*

Complex **4** crystallizes in the orthorhombic space group Pbcn, and the molecular structure reveals a salt resulting from a four-electron reduction process (Fig. 4). The molecular structure of **4** represents a rare example of a titanium alkylidene-ate complex [36]. Imide formation is clearly observable from the short Ti(1)–N(26) distance (1.798(2) Å) and linear angle (Ti(1)–N(26)–C(27), 177.6(1)°). However, clear discrepancies are evident in the NCCC ring metrical parameters of **4** when compared to neutral analogues **1** and **3** (Table 2). For example, the Ti atom deviates significantly from the NCCC imaginary plane (~0.33 Å), while the Ti–C_α distance in **4** is shorter than that observed for the Ti–C_{vinyl} distances for both **1** and **3** (Table 2). Dipping of the Ti atom from the NCCC imaginary plane is further manifested by the close interaction of the metal center with the two β-C atoms composing the ring (Ti(1)–C(3), 2.442(4) Å; Ti(1)–C(3), 2.340(5) Å). Likewise, the C_β–C_β distance of the NCCC framework in **4** is shorter than that observed for the structure of **1** and **3**. Consequently, the latter feature makes the adjacent C_α-C_β and C_β-N linkages elongated when compared to same parameters in the solid state structure of **1** and **3**. The molecular structure of **4** also reveals the lithium counter cation interacting with the alkylidene carbon (2.300(3) Å) and the imide nitrogen (2.071(3) Å), thereby hinting that the charge in the metal complex is likely delocalized about the C(5)–Ti(1)–N(26) atoms (Scheme 2). If one ignores the two Ti–C_β interactions, an Et_2O molecule occupies the fourth coordination site in the solid state structure of **4** (Ti(1)–O(39), 2.117(1) Å).

3. Experimental

3.1. *General considerations*

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard



Scheme 2.

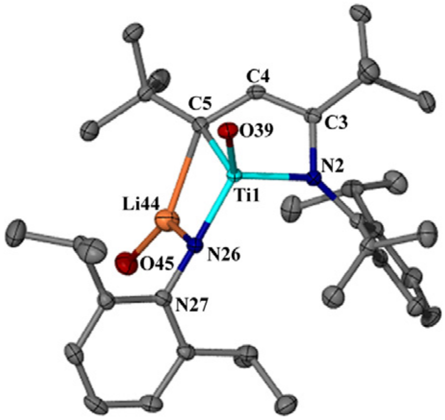


Fig. 4. Molecular structure of **4** displaying thermal ellipsoids at the 50% probability level with distances reported in (Å) and angles in (°). All H-atoms and ethyl groups on the two oxygen atoms have been omitted for clarity. Crystallographic and refinement data are displayed in Table 1 and selected metrical parameters are displayed in Table 2.

Schlenk techniques under an argon atmosphere [37]. Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column [38]. Diethylether was dried by passage through a column of activated alumina [38]. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a dry box. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed and dried over CaH_2, then vacuum transferred to 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. (nacnac)$TiCl_2$ [12b] (nacnac$^-$ = $[ArNC(^tBu)]_2CH$, Ar = 2,6-$^iPr_2C_6H_3$), KC_8, [33] were prepared according to the literature. LiNHAr (Ar = 2,6-$^iPr_2C_6H_3$) was prepared from the addition of ^{n}BuLi to H_2NAr in hexanes at −35 °C. ^{t}BuLi was recrystallized from pentane at −78 °C, and stored cold. All other chemical were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ. ^{1}H, and ^{13}C NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm and 128.0 ppm). Solution magnetic moments were obtained by the method of Evans [39]. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures [40,41].

3.2. Synthetic procedures

3.2.1. Synthesis of (ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(THF)Cl (1)

In a vial was dissolved (nacnac)$TiCl_2$ (300 mg, 0.48 mmol) in toluene (10 mL) and the solution was cooled to −35 °C. To the solution was added a cold THF (5 mL) suspension containing KC_8 (71.9 mg, 0.53 mmol). The solution was allowed to stir for 5 min, filtered and then dried in vacuo. The red residue was extracted with Et_2O and filtered. The resulting filtrate was concentrated and cooled to −35 °C to yield red crystals of (ArN(^{t}Bu)-CCHC(^{t}Bu))Ti=NAr(THF)Cl (**1**) (214 mg, 0.32 mmol, 67% yield). ^{1}H NMR (23°C, 399.8 MHz, C_6D_6): δ 7.04–6.82 (m, 7 H, Ar-*H*, ArN(^{t}Bu)CC*H*C(^{t}Bu)), 4.79 (septet, 2 H, C*H*Me$_2$), 3.56 (br, 4 H, THF), 3.52 (septet, 1 H, C*H*Me$_2$), 2.88 (septet, 1 H, C*H*Me$_2$), 1.56 (s, 9 H, ArN(^{t}Bu)CCHC(^{t}*Bu*)) 1.46 (d, 6 H, CH*Me*$_2$)s, 1.36 (d, 6 H, CH*Me*$_2$), 1.26 (d, 3 H, CH*Me*$_2$), 1.25 (d, 3 H, CH*Me*$_2$), 1.22 (m, 4 H, THF), 1.09 (d, 3 H, CH*Me*$_2$), 1.06 (d, 3 H, CH*Me*$_2$), 1.04 (s, 9 H, ArN(^{t}*Bu*)CCHC(^{t}Bu)). ^{13}C NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 258.9 (ArN(^{t}Bu)CCH*C*(^{t}Bu)), 193.3 (ArN(^{t}Bu)*C*CHC(^{t}Bu)), 158.3, 144.9, 144.7, 141.9, 141.4, 127.9, 126.6, 124.3, 123.6, 122.9, 122.3, 73.54 (THF), 43.53 (ArN(CMe$_3$)CCHC(*C*Me$_3$)), 43.24 (ArN(*C*Me$_3$)CCHC(CMe$_3$)), 31.01 (ArN(CMe$_3$)CCHC(C*Me*$_3$)), 30.14 (ArN(C*Me*$_3$)CCHC(CMe$_3$)), 28.65 (*C*HMe$_2$), 28.09 (THF), 27.20 (*C*HMe$_2$), 26.04 (*C*HMe$_2$), 25.42 (*Me*), 24.91 (*Me*), 24.83 (*Me*), 24.70 (*Me*), 24.25 (*Me*), 23.22 (*Me*). *Anal.* Calc. for C$_{39}$H$_{61}$N$_2$OClTi: C, 71.27; H, 9.35; N, 4.26. Found: C, 71.54; H, 9.33; N, 4.56%.

*3.2.2. Synthesis of (nacnac)Ti(NHAr)Cl (**2**)*

In a flask was dissolved (nacnac)TiCl$_2$ (500 mg, 0.80 mmol) in toluene and the solution was cooled to −35 °C. To the cold solution was added dropwise a cold toluene (20 mL) solution containing Li(NHAr) (144.7 mg, 0.79 mmol). The solution was allowed to stir for 2 h, filtered, and then dried in vacuo. The green residue was extracted with Et$_2$O and filtered. The resulting filtrate was concentrated and cooled to −35 °C to yield green crystals of (nacnac)Ti(NHAr)Cl (**2**) (521 mg, 0.68 mmol, 85% yield). ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 11.5 ($\Delta v_{1/2} = 16$ Hz), 5.73 ($\Delta v_{1/2} = 32$ Hz), 5.56 ($\Delta v_{1/2} = 25$ Hz), 5.41 ($\Delta v_{1/2} = 24$ Hz), 4.54 ($\Delta v_{1/2} = 34$ Hz), 3.69 ($\Delta v_{1/2} = 57$ Hz), 2.61 ($\Delta v_{1/2} = 26$ Hz), 1.70 ($\Delta v_{1/2} = 30$ Hz), 1.35 ($\Delta v_{1/2} = 105$ Hz). $\mu_{\mathrm{eff}} = 1.88\,\mu_{\mathrm{B}}$ (C$_6$D$_6$, 298 K Evans' method). *Anal.* Calc. for C$_{47}$H$_{71}$N$_3$ClTi: C, 74.14; H, 9.40; N, 5.52. Found: C, 74.29; H, 8.92; N, 5.60%.

*3.2.3. Synthesis of (ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(NHAr) (**3**)*

In a vial was dissolved **2** (193 mg, 0.25 mmol) in toluene (10 mL) and the solution was cooled to −35 °C. To the solution was added a cold THF (5 mL) suspension containing KC$_8$ (37.7 mg, 0.28 mmol). The solution was allowed to stir for 20 min, filtered and then dried in vacuo. The red residue was extracted with Et$_2$O and filtered. The resulting filtrate was concentrated and cooled to −35 °C to yield red crystals of (ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(NHAr) (**3**) (162 mg, 0.22 mmol, 88% yield). ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.16–6.78 (m, 10 H, Ar-*H*, ArN(^{t}Bu)CC*H*C(^{t}Bu)), 4.32 (br, 2 H, C*H*Me$_2$), 3.65 (septet, 1 H, C*H*Me$_2$), 3.21 (septet, 2 H, C*H*Me$_2$), 2.88 (septet, 1 H, C*H*Me$_2$), 1.29–1.12 (36 H, ArN(^{t}Bu)CCHC(^{t}*Bu*) and CH*Me*$_2$), 1.06–1.02 (12 H, ArN(^{t}*Bu*)CCHC(^{t}Bu) and CH*Me*$_2$), 1.00 (d, 6 H, CH*Me*$_2$). The N*H* resonance was not located in the ^{1}H NMR spectrum. ^{13}C NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 250.4 (ArN(^{t}Bu)CCH*C*(^{t}Bu)), 188.6 (ArN(^{t}Bu)*C*CHC(^{t}Bu)), 159.6, 149.4, 140.8, 140.3, 140.1, 136.9, 124.8, 124.5, 122.9, 122.2, 123.0, 121.2, 120.9, 43.44 (ArN(CMe$_3$)CCHC(*C*Me$_3$)), 41.88 (ArN(*C*Me$_3$)CCHC(CMe$_3$)), 30.40 (ArN(CMe$_3$)CCHC(C*Me*$_3$)), 30.35 (*C*HMe$_2$), 29.06 (ArN(C*Me*$_3$)CCHC(CMe$_3$)), 28.79 (*C*HMe$_2$), 28.51 (*C*HMe$_2$), 27.73 (*C*HMe$_2$), 25.78 (*Me*), 24.28 (*Me*), 23.86 (*Me*), 23.76 (*Me*), 23.69 (*Me*), 23.53 (*Me*). *Anal.* Calc. for C$_{47}$H$_{71}$N$_3$Ti: C, 77.76; H, 9.86; N, 5.79. Found: C, 77.48; H, 9.79; N, 5.47%.

3.2.4. Synthesis of [Li(Et$_2$O)][(ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(Et$_2$O)] (4)

In a vial was suspended (nacnac)TiCl$_2$ (200 mg, 0.32 mmol) in pentane (10 mL) and the solution was cooled to −35 °C. To the solution was added a cold solution of ^{t}BuLi (63.2 mg, 0.99 mmol) followed by 6 drops of Et$_2$O. The solution was allowed to stir for 2 h. The resulting solution was filtered, and the filtrate was concentrated and cooled to −35 °C to yield red crystals of [Li(Et$_2$O)][(ArN(^{t}Bu)CCHC(^{t}Bu))Ti=NAr(Et$_2$O)] (**4**) (184 mg, 0.26 mmol, 81% yield). ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.39–6.99 (m, 6 H, Ar-*H*), 6.88 (s, ArN(^{t}Bu)CC*H*C(^{t}Bu)), 3.89 (septets, 1 H, C*H*Me$_2$), 3.49–3.19 (m, 10 H, C*H*Me$_2$, Et$_2$O), 2.88 (septet, 1 H, C*H*Me$_2$), 1.72 (s, 9 H, ArN(^{t}Bu)CCHC(^{t}*Bu*)), 1.58–1.54 (overlapping doublets, 12 H, CH*Me*$_2$), 1.35 (s, 9 H, ArN(^{t}*Bu*)CCHC(^{t}Bu)), 1.09–0.84 (24 H, Et$_2$O and CH*Me*$_2$). ^{13}C NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 210.5 (ArN(^{t}Bu)CCH*C*(^{t}Bu)), 157.1 (ArN(^{t}Bu)*C*CHC(^{t}Bu)), 152.6 (*C*$_6$H$_3$), 142.3 (*C*$_6$H$_3$), 140.2 (*C*$_6$H$_3$), 139.5 (*C*$_6$H$_3$), 125.4 (*C*$_6$H$_3$), 123.9 (*C*$_6$H$_3$), 122.7 (*C*$_6$H$_3$), 116.9 (*C*$_6$H$_3$), 116.4 (*C*$_6$H$_3$), 102.6 (ArN(^{t}Bu)C*C*HC(^{t}Bu)), 66.17 (Et$_2$O), 63.78 (Et$_2$O), 42.32 (ArN(CMe$_3$)CCHC(*C*Me$_3$)), 39.30 (ArN(*C*Me$_3$)CCHC(CMe$_3$)), 33.21 (ArN(CMe$_3$)CCHC(C*Me*$_3$)), 32.76 (ArN(C*Me*$_3$)CCHC(CMe$_3$)), 28.57 (*C*HMe$_2$), 26.64 (*C*HMe$_2$), 26.47 (*C*HMe$_2$), 25.45 (*Me*), 24.89 (*Me*), 24.76 (*Me*), 23.96 (*Me*), 13.94 (Et$_2$O), 12.85 (Et$_2$O). *Anal.* Calc. for C$_{43}$H$_{73}$N$_2$O$_2$LiTi: C, 73.27; H, 10.44; N, 3.97. Found: C, 73.11; H, 10.25; N, 4.25%.

3.3. Crystallographic details

Inert atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.1 mm) and mounted on a SMART6000 (Bruker) at 119 K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20–30 frames. Data collection were carried out using graphite monochromated Mo Kα radiation with a frame time of 5–30 s with a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT) [40]. The structure was solved using SHELXS-97 and refined with SHELXL-97 [41]. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified, *vide supra*). A summary of crystal data and refinement details for all structures are given in Table 2.

4. Conclusions

One- or three-electron reduction reactions involving Ti(III) systems bearing the β-diketiminate ligand nacnac ($\text{nacnac}^- = [\text{ArNC}(^t\text{Bu})]_2\text{CH}$, $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) result in C–N bond rupture concomitant with formation of monanionic azabutadienyl and alkylidene-anilide frameworks, respectively. In these types of reactions, a Ti(II) intermediate appears reasonable to propose, and such species is likely responsible for C–N bond rupture of the β-diketiminate ligand NCCCN backbone. Therefore, the following work demonstrates that β-diketiminate are excellent imide and alkylidene synthons when incorporated with low-valent early transition metals.

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Appendix A. Supplementary data

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre, CCDC Nos. 610957–610960. Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.07.045.

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