

## Communication

## Organometallic consequences of a redox reaction: Terminal trimethylsilylmethylidene titanium complexes prepared by a one-electron oxidation step

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## Abstract

One-electron oxidation of the titanium(III) bis-trimethylsilylmethyl complex  $(\text{nacnac})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$  (**1**) ( $\text{nacnac}^- = [\text{ArNC}(\text{Me})_2\text{CH}]$ ,  $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ), readily prepared from  $(\text{nacnac})\text{TiCl}_2(\text{THF})$  and 2 equiv. of  $\text{LiCH}_2\text{SiMe}_3$  in  $\text{Et}_2\text{O}$ , with  $\text{AgOTf}$  results in formation of the five-coordinate and terminal titanium alkylidene complex  $(\text{nacnac})\text{Ti}=\text{CHSiMe}_3(\text{OTf})(\text{THF})$  (**2**)-THF concurrent with extrusion of tetramethylsilane and precipitation of silver metal. Complex **2**-THF eliminates THF slowly under dynamic vacuum to generate the four-coordinate alkylidene **2** along with some decomposition products. Alternatively, the four-coordinate and non-solvento alkylidene complex, **2**, can be prepared from **1** and  $\text{AgOTf}$  in pentane. Complex **2** undergoes cross-metathesis transformation to afford  $[\text{ArNC}(\text{Me})\text{CHC}(\text{Me})=\text{CHSiMe}_3]\text{Ti}=\text{NAr}(\text{OTf})$  (**3**) as the major product after 34 h at room temperature. Complexes **1**, **2**, **2**-THF, and **3** have been fully characterized spectroscopically, and single crystal X-ray diffraction analysis for **1** and **2**-THF are presented. © 2007 Elsevier B.V. All rights reserved.

*Keywords:* Alkyl; Alkylidene; Oxidation; Titanium complexes; X-ray structure

## 1. Introduction

High-oxidation state transition metal complexes of groups such as 5 [1–7], 6 [8–13,2,14] and 7 [2] share a common ground in stabilizing the terminal trimethylsilylmethylidene ligand ( $\text{M}=\text{CHSiMe}_3$ ) [2,15,16]. However, the number of terminal trimethylsilylmethylidene metal complexes plummets dramatically when the metal in question represents the lighter congener for each group (e.g., Ti, V, Cr) [2,15–18]. In contrast, group 4 transition metal compounds bearing the terminal trimethylsilylmethylidene ligand are even more scant, with the only reported examples (isolable) being the titanium and zirconium complexes  $(\text{PNP})\text{Ti}=\text{CHSiMe}_3(\text{X})$  ( $\text{PNP}^- = \text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2$ ) [19–22];  $\text{X}^- = \text{OTf}$  [23],  $\text{CH}_2\text{SiMe}_3$  [17]) and

$[\text{C}_5\text{H}_3(\text{SiMe}_2\text{P}^i\text{Pr}_2)_2]\text{Zr}=\text{CHSiMe}_3(\text{Cl})$  [24,25], respectively. In most cases, the  $\text{M}=\text{CHSiMe}_3$  functionality in question must be trapped or generated in situ, to avoid decomposition pathways from occurring [26–29]. In rare cases however, dimers arise from bridging of the trimethylsilylmethylidene unit [30,31]. Hence, the relatively few examples of group 4 alkylidene complexes bearing the trimethylsilyl group is surprising since the sterically demanding alkyl reagent  $\text{LiCH}_2\text{SiMe}_3$  is both commercially available and affordable much more so than the corresponding salts  $\text{LiCH}_2^t\text{Bu}$  [32],  $\text{LiCH}_2\text{CMe}_2\text{Ph}$  [33], and  $\text{LiCH}_2\text{Ph}$  [34]. Likewise, nucleophilic charge at the  $\alpha$ -alkylidene carbon should be expected to be lower given the inherent electron withdrawing effect of trimethylsilyl group and sigma-hyperconjugation.

In this manuscript we report a facile synthetic route to low-coordinate and terminal titanium complexes possessing the terminal trimethylsilylmethylidene motif, namely the compounds  $(\text{nacnac})\text{Ti}=\text{CHSiMe}_3(\text{OTf})(\text{THF})$  and its

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non-solvento, four-coordinate counterpart (nacnac)Ti=CHSiMe<sub>3</sub>(OTf) (nacnac<sup>-</sup> = [ArNC(Me)]<sub>2</sub>CH, Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [35]. Our strategy involves a one-electron oxidation reaction of a Ti(III) bis-alkyl precursor (nacnac)Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> to promote the  $\alpha$ -hydrogen abstraction step.

The only examples of a titanium complexes bearing the terminal trimethylsilylmethylidene unit were recently reported by us, and involved the compounds (PNP)Ti=CHSiMe<sub>3</sub>(X) (X<sup>-</sup> = OTf [23], CH<sub>2</sub>SiMe<sub>3</sub> [17]). Rothwell and co-workers have reported bridging trimethylsilylmethylidene complexes of titanium [30,31]. In their case, dimerization presumably occurs due to the unsaturated nature of the putative, three-coordinate Ti(IV) complex, in combination with the unhindered composition of the supporting ancillary ligand [30,31]. In the case of terminal and stable titanium trimethylsilylmethylidene complexes, spectroscopic discrepancies arise when these ligands are compared to the C-based neopentylidene analogues. When measured up against (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu), the alkylidene carbon resonance for (PNP)Ti=CHSiMe<sub>3</sub>(CH<sub>2</sub>SiMe<sub>3</sub>) (310.5 ppm) shifts further downfield in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ( $\Delta$  = 50.5 ppm) [17]. This parameter reflects the electronic effect imposed by the trimethylsilyl unit on the  $\alpha$ -C. In addition, the *J*<sub>C-H</sub> of 99 Hz (vs. 86 Hz for (PNP)Ti=CH<sup>t</sup>Bu(CH<sub>2</sub><sup>t</sup>Bu)) lends support for the trimethylsilylmethylidene complex having a weaker  $\alpha$ -hydrogen agostic interaction taking place with the Ti(IV) center. This implies then that the Ti(IV) center is more electron rich when supported by a trimethylsilylmethylidene ligand as opposed to the neopentylidene motif (the role of steric effects might also be contributing to this parameter and we cannot discard this possibility). Therefore, the above spectroscopic features arguably imply that the Ti=CHSiMe<sub>3</sub> derivative is less electron hungry than the Ti=CH<sup>t</sup>Bu, which is a dichotomy considering the relative few examples reported for the former system.

Our approach into incorporating the trimethylsilylmethylidene ligand onto Ti(IV) involved a similar protocol for the synthesis of (nacnac)Ti=CH<sup>t</sup>Bu(OTf) [36]. Accordingly, complex (nacnac)TiCl<sub>2</sub>(THF) [36] can be readily alkylated with LiCH<sub>2</sub>SiMe<sub>3</sub> to afford green-blue crystals of (nacnac)Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**1**) in 73% isolated yields upon work-up of the reaction mixture (Scheme 1). Complex **1**

displays a magnetic moment of 1.91  $\mu_B$  thus consistent with a d<sup>1</sup> electronic configuration. In order to establish an accurate connectivity for **1**, we collected single crystal X-ray diffraction data. Consequently, complex **1** crystallizes in the Monoclinic space group *P2(1)/n*, and as indicated in Fig. 1, the molecule structure adopts a pseudo tetrahedral geometry whereby the  $\beta$ -diketiminato ligand occupies the remaining two coordination sites. The Ti–C distances (2.104(3) and 2.139(3) Å) are within range to similar bis-alkyl titanium complexes reported by us [36–38] and Budzelaar and co-workers [39]. Although all hydrogens in the molecule were located and refined isotropically, their location does not suggest an  $\alpha$ -hydrogen agostic interaction taking place with the Ti(III) center. The Ti center in **1** deviates 0.601 Å out of the imaginary NCCCN plane. Each flanking aryl group bound to the  $\alpha$ -nitrogens is oriented perpendicular to the N–Ti–N plane, placing the sterically

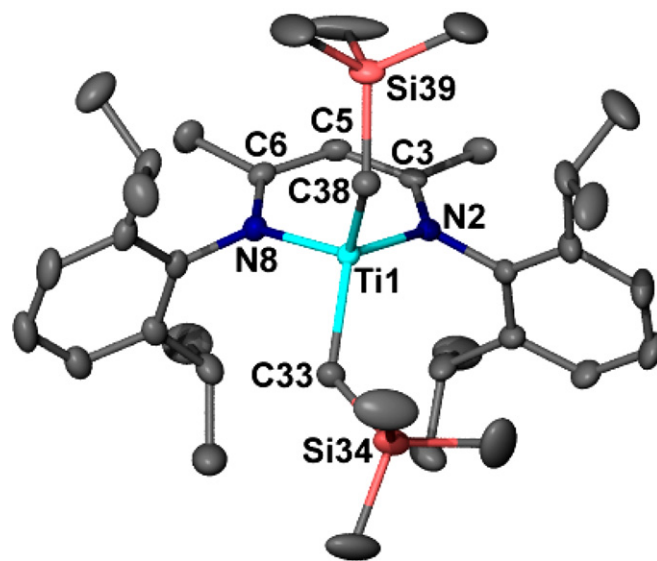
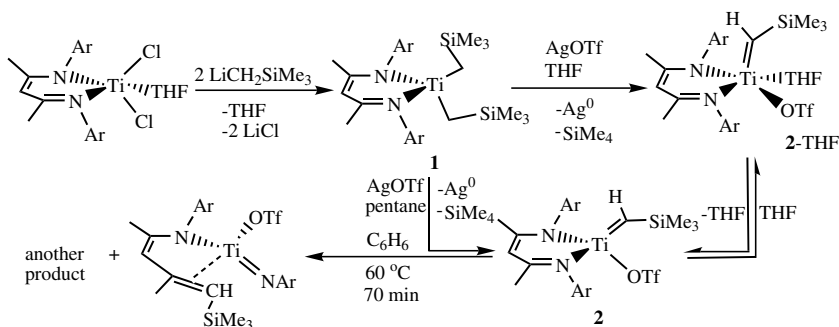


Fig. 1. Molecular structure of **1** displaying thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for the purpose of clarity. Selected metrical parameters are reported in Å (distances) and ° (angles). Ti1–C33, 2.104(3); Ti1–C38, 2.139(3); Ti1–N2, 2.017(1); Ti1–N8, 2.033(1); N2–C3, 1.354(5); C3–C5, 1.396(8); C5–C6, 1.405(8); C6–N8, 1.348(5); Ti1–C33–Si34, 130.72(7); Ti1–C38–Si39, 125.85(7); N8–Ti1–N2, 91.95(4); C38–Ti1–C33, 109.62(5); C38–Ti1–N2, 112.58(5); C38–Ti1–N8, 118.65(5); C33–Ti1–N2, 118.46(5); C33–Ti1–N8, 104.81(5).



Scheme 1.

hulking isopropyl groups up and down relative to the TiNCCCN framework. Consequently, this feature maximizes steric repulsion with the trimethylsilyl group, hence making these ligands orient opposite of each other and in one direction (propeller-like fashion). A selected list of metrical parameters for the molecular structure of **1** are displayed with Fig. 1.

In the absence of oxidants or moisture, compound **1** is remarkably stable. However, exposure of **1** to an oxidant such as AgOTf in THF evinces an immediate color change from blue-green to red-brown concurrent with formation of Ag<sup>0</sup> mirror. Filtration of the metal, and subsequent work-up of the reaction mixture results in the isolation of brown blocks of the trimethylsilylmethylidene complex (nacnac)Ti=CHSiMe<sub>3</sub>(OTf)(THF) (**2**)-THF (Scheme 1). The <sup>1</sup>H NMR spectrum of **2**-THF reveals a highly downfield  $\alpha$ -alkylidene hydrogen resonance at 12.30 ppm as well as a complex retaining an equivalent of THF. In addition, the <sup>13</sup>C NMR spectrum clearly exposes a highly deshielded alkylidene carbon resonance at 319.4 ppm with a  $J_{C-H}$  component of 106 Hz. This latter feature suggests moderate  $\alpha$ -hydrogen agostic interaction taking place with the metal center and presents **2**-THF to be less electrophilic at Ti(IV), when compared to (nacnac)Ti=CH<sup>t</sup>Bu(OTf) ( $J_{C-H}$  = 96 Hz) [38,36]. Formation of a OTf<sup>-</sup> complex in **2**-THF is also evident from the <sup>19</sup>F NMR spectrum (singlet resonance at -77.8 ppm). We speculated whether complex **2**-THF possessed a smaller  $\alpha$ -hydrogen agostic interaction due to higher coordination number at Ti(IV) via binding of THF to the metal center. With this hypothesis in mind, complex **2**-THF was subjected to dynamic vacuum over several hours, with only partial elimination of THF (20% conversion to a new product after 24 h), which we attribute to the low-coordinate species (nacnac)Ti=CHSiMe<sub>3</sub>(OTf) (**2**) (Scheme 1). Solutions of **1** also decompose at room temperature and in the absence of dynamic vacuum. However, solutions of **2** were marred with content of starting material, in addition to two new decomposition products (vide infra). Independently, complex **2** can be generated cleanly, via one-electron oxidation of **1** with AgOTf in pentane (76% isolated yield, Scheme 1). <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra are essentially analogous to its solvated counterpart, **2**-THF. Despite this similarity, the <sup>1</sup>H NMR spectrum shows a slight deviation in the chemical shift for the alkylidene hydrogen (12.39 ppm), while the <sup>13</sup>C NMR spectrum displays a further downfield chemical shift at 320.1 ppm, congruently with a stronger Ti...H  $\alpha$ -hydrogen agostic interaction (when compared to **2**-THF) taking place with the four-coordinate metal center ( $J_{C-H}$  = 98 Hz) [38,36]. This feature implies that coordination of THF is not a necessity for the stability of **2**, and that binding of the Lewis base to the Ti(IV) center reduces the  $\alpha$ -hydrogen agostic interaction. As anticipated, addition of THF to **2** rapidly generates **2**-THF quantitatively (Scheme 1).

As observed with **2**-THF, complex **2** also decomposes in solution at room temperature over 34 h. We have deter-

mined one of the compounds resulting from solution decomposition of **2** and found it to be the cross-metathesis product [ArNC(Me)CHC(Me)=CHSiMe<sub>3</sub>]Ti=NAr(OTf) (**3**) along with another species (which we have not identified) in a 3:1 ratio, respectively (Scheme 1). Based on <sup>1</sup>H NMR spectra, the latter product does not appear to be the intramolecular double C-H metallated product: an analogous byproduct formed from the decomposition of (nacnac)Ti=CH<sup>t</sup>Bu(OTf), namely the complex Ti(OTf){[2,6-(CMe<sub>2</sub>)(CHMe<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>]NC(Me)}<sub>2</sub>CH [38,36]. We do however, observe SiMe<sub>4</sub> in the mixture, but have not been able to separate the second metal-based product. Separation of **3** was achieved by extracting the reaction mixture with hexane, filtering, and crystallizing the filtrate at -35 °C. Formation of compound **3** is supported by a combination of <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra as well as comparison of its spectral shifts with the previously reported analogue [ArNC(Me)CHC(Me)=CH<sup>t</sup>Bu]Ti=NAr(OTf) [38,36]. Our earlier reports revealed that complex (nacnac)Ti=CH<sup>t</sup>Bu(OTf) had an estimated  $t_{1/2}$  of 45 min at 57 °C and that complete decomposition typically occurred over ~2 h [38,36]. In comparison, compound **2** transforms at room temperature over a period of 34 h and decomposes completely within 70 min at 60 °C. Therefore, it appears that the titanium trimethylsilylmethylidene is thermally less stable than the neopentylidene derivative, but not significantly. This implies that complex **2**, despite having a more delocalized charge at the alkylidene carbon, might display enhanced reactivity given the more exposed nature of the alkylidene unit. The latter property could facilitate faster intramolecular cross-metathesis of the alkylidene with the nacnac imine residue more than with the bulkier neopentylidene ligand.

Single crystal X-ray analysis of **2**-THF clearly exposes a rare example of a five-coordinate titanium complex bearing a terminal trimethylsilylmethylidene functionality (Ti=C, 1.863(3) Å, Fig. 2). Binding of a THF ligand is also evident (Ti-O, 2.155(2) Å) thus resulting in a pseudo square pyramid geometry at titanium, whereby the alkylidene moiety occupies the axial position. The Ti atom sits ~0.448 Å above the mean plane defined by the  $\beta$ -diketiminato nitrogens, and the THF and OTf<sup>-</sup> oxygen atoms. Distortion about the trimethylsilylmethylidene unit is clearly evident from the obtuse Ti-C-Si angle of 156.4(2)°, which is also diagnostic of **2**-THF enjoying from an  $\alpha$ -hydrogen agostic interaction. Coordination of THF renders the system C<sub>1</sub> symmetric in the solid state structure. However, the solution NMR (<sup>1</sup>H and <sup>13</sup>C, vide supra) spectrum of **2**-THF is consistent with this system having C<sub>s</sub> symmetry thus implying that a rapid fluxional process by which THF dissociates in solution, might be operational. Other salient parameters associated with the solid state structure of **2**-THF are shown with Fig. 2.

The two alkylidene systems presented here represent a new class of titanium trimethylsilylmethylidene complexes that can be readily assembled by a facile one-electron oxidatively induced  $\alpha$ -hydrogen abstraction reaction

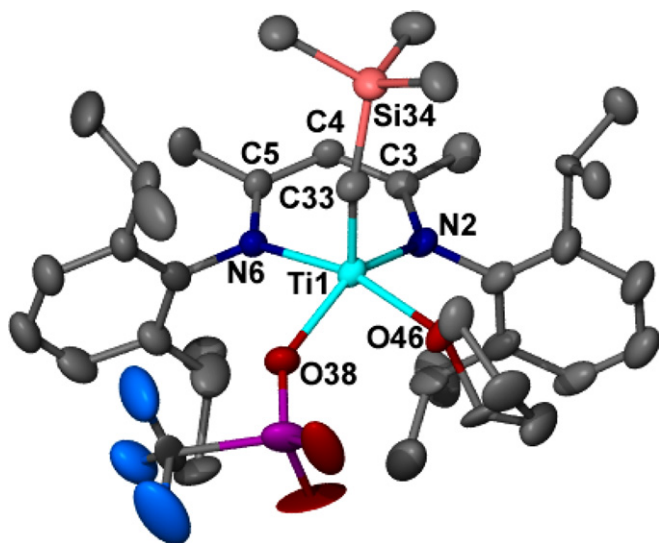


Fig. 2. Molecular structure of **2-TiHf** displaying thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for the purpose of clarity. Selected metrical parameters are reported in Å (distances) and ° (angles). Ti1–C33, 1.863(3); Ti1–O46, 2.155(2); Ti1–N2, 2.048(2); Ti1–N6, 2.136(2); Ti1–O38, 2.073(2); N2–C3, 1.363(4); C3–C4, 1.378(4); C4–C5, 1.402(4); C5–N6, 1.331(3); Ti1–C33–Si34, 156.4(2); N6–Ti1–N2, 89.05(9); O38–Ti1–C33, 111.9(2); O38–Ti1–N2, 143.72(9); O38–Ti1–N6, 85.43(8); O38–Ti1–O46, 83.07(8); O46–Ti1–N2, 93.99(9); O46–Ti1–N6, 164.40(9); O46–Ti1–C33, 95.2(1); C33–Ti1–N2, 104.4(2); C33–Ti1–N6, 98.9(1).

[15,16,40]. Depending on the nature of the solvent (THF vs. pentane), higher coordination numbers about the metal center can be conveniently suppressed. Consequently, the lower coordination number results in a more electron deficient metal center, and an enhanced interaction of the metal with the  $\alpha$ -hydrogen on the alkylidene ligand. Given the unsaturated nature and oxophilicity of the titanium presented here, compounds such as **2** and **2-TiHf** might be excellent scaffolds for olefin metathesis or Wittig-like transformations [28], and we are currently exploring their reaction potential.

## 2. Experimental

### 2.1. 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 Schlenk techniques under an argon atmosphere. 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 [41]. Diethylether was dried by passage through a column of activated alumina [41]. 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 transferred into a dry box.  $C_6D_6$  was purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. Celite, alumina, and

4 Å molecular sieves were activated under vacuum overnight at 200 °C.  $Li(nacnac)[35]$  ( $nacnac^- = [ArNC(Me)_2CH$ ,  $Ar = 2,6\text{-}iPr_2C_6H_3$ ) and  $(nacnac)TiCl_2(THF)$  [39,36] were prepared according to the literature.  $LiCH_2SiMe_3$  was purchased from Aldrich in a pentane solution, filtered, concentrated and cooled to  $-35$  °C to afford white crystals of the alkyl reagent. All other chemical were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ.  $^1H$ ,  $^{13}C$ ,  $^{19}F$ , and  $^{31}P$  NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers.  $^1H$  and  $^{13}C$  NMR are reported with reference to solvent resonances (residual  $C_6D_5H$  in  $C_6D_6$ , 7.16 ppm and 128.0 ppm).  $^{19}F$  NMR chemical shifts are reported with respect to external  $HOCOFC_3$  ( $-78.5$  ppm). Solution magnetization measurements were determined by the method of Evans [42,43]. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of  $N_2$  (g) at low temperatures [44,45].

### 2.2. Preparation of $(nacnac)Ti(CH_2SiMe_3)_2$ (**1**)

In a round bottom flask was suspended  $(nacnac)TiCl_2(THF)$  [300 mg, 0.49 mmol] in  $Et_2O$  (50 mL) and the solution was cooled to  $-35$  °C. To the cold solution was added an equally cold  $Et_2O$  ( $\sim 20$  mL) solution containing  $LiCH_2SiMe_3$  [95.2 mg, 1.01 mmol]. After stirring for 5 h the blue-green solution was filtered and dried in vacuo. The filtrate residue was dissolved in pentane and re-filtered. The pentane filtrate was reduced in volume and cooled to  $-35$  °C to afford **1** as dark blue-green crystals [233 mg, 0.36 mmol, 73% yield]. For **1**:  $^1H$  NMR ( $C_6D_6$ , 300.1 MHz, 25 °C):  $\delta$  5.64 ( $\Delta v_{1/2} = 21$  Hz), 5.26 ( $\Delta v_{1/2} = 18$  Hz), 3.09 ( $\Delta v_{1/2} = 28$  Hz), 2.78 ( $\Delta v_{1/2} = 63$  Hz),  $-0.11$  ( $\Delta v_{1/2} = 38$  Hz). Evans Magnetic Moment ( $C_6D_6$ , 298 K):  $\mu_{eff} = 1.91 \mu_B$ . Anal. Calc. for  $C_{37}H_{63}N_2Si_2Ti$ : C, 69.44; H, 9.92; N, 4.38. Found: C, 69.08; H, 9.71; N, 4.46%.

### 2.3. Preparation of $(nacnac)Ti = CHSiMe_3(OTf)(THF)$ (**2**)-THF

In a scintillation vial was dissolved **1** [100 mg, 0.16 mmol] in THF (10 mL) and the solution was cooled to  $-35$  °C. To the cold blue-green solution was added a cold ( $-35$  °C) THF (5 mL) solution of  $AgOTf$  [40.95 mg, 0.16 mmol] which caused a rapid color change to red-brown concurrent with formation of a silver mirror. The solution was stirred for 30 min and filtered. The filtrate was then dried in vacuo and dissolved in pentane. This was followed by filtration, and the resulting red-brown solution was reduced in volume under vacuo and cooled to  $-35$  °C to yield **2-TiHf** as dark blocks [98 mg, 0.13 mmol, 81% yield]. For **2-TiHf**:  $^1H$  NMR (23 °C, 399.8 MHz,  $C_6D_6$ ):  $\delta$  12.30 (s, 1H,  $Ti=CHSiMe_3$ ), 7.20–7.14 (m, 6H,  $ArH$ ), 4.86 (s, 1H,  $ArN(Me)CCHC(Me)NAr$ ), 3.64 (br, 4H, THF), 3.47 (septet, 2H,  $CHMe_2$ ), 2.86 (septet, 2H,  $CHMe_2$ ), 1.63 (d, 6H,  $CHMe_2$ ), 1.49 (s, 6H,  $ArN$

(*Me*)CCHC(*Me*)NAr), 1.45 (br, 4H, THF), 1.39 (d, 6H, CHMe<sub>2</sub>), 1.29 (d, 6H, CHMe<sub>2</sub>), 1.10 (d, 6H, CHMe<sub>2</sub>), -0.25 (s, 9H, Ti=CHSiMe<sub>3</sub>). <sup>13</sup>C NMR (23 °C, 100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 319.4 (Ti=CHSiMe<sub>3</sub>, J<sub>C-H</sub> = 106 Hz), 167.7 (ArN(*Me*)CCHC(*Me*)NAr), 145.3 (C<sub>6</sub>H<sub>3</sub>), 142.8 (C<sub>6</sub>H<sub>3</sub>), 140.5 (C<sub>6</sub>H<sub>3</sub>), 124.6 (C<sub>6</sub>H<sub>3</sub>), 124.5 (C<sub>6</sub>H<sub>3</sub>), 96.77 (ArN(*Me*)CCHC(*Me*)NAr), 69.14 (THF), 30.17 (CHMe<sub>2</sub>), 28.82 (CHMe<sub>2</sub>), 27.51 (THF), 25.80 (*Me*), 24.72 (*Me*), 24.54 (*Me*), 24.44 (*Me*), 23.67 (*Me*), 0.80 (Ti=CH-SiMe<sub>3</sub>). <sup>19</sup>F NMR (23 °C, 282.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -77.76 (s, TiO<sub>3</sub>SCF<sub>3</sub>). Anal. Calc. for C<sub>38</sub>H<sub>59</sub>N<sub>2</sub>SiO<sub>4</sub>SF<sub>3</sub>Ti : C, 59.04; H, 7.69; N, 3.62. Found: C, 58.96; H, 7.89; N, 3.63%.

#### 2.4. Preparation of (*nacnac*)Ti=CHSiMe<sub>3</sub>(OTf) (2)

In a vial was dissolved **1** [215 mg, 0.33 mmol] in pentane (10 mL) and the solution was cooled to -35 °C. To the blue-green solution was added solid AgOTf [103.58 mg, 0.40 mmol] causing a color change to red-brown with formation of silver metal. The solution was stirred for 45 min. The solution was then filtered and the resulting red-brown filtrate solution was reduced in volume under vacuo, and cooled to -35 °C to yield **2** as dark crystals [176 mg, 0.25 mmol, 76% yield]. Note: Complex **2** can be generated from the evacuation of **2**-THF, albeit at a very slow rate (after 24 h only 20% conversion occurred). Complete conversion of **2**-THF to **2** is never observed. For **2**: <sup>1</sup>H NMR (23 °C, 399.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 12.39 (s, 1H, Ti=CH-SiMe<sub>3</sub>), 7.20–7.09 (m, 6H, ArH), 4.77 (s, 1H, ArN(*Me*)CCHC(*Me*)NAr), 3.39 (septet, 2H, CHMe<sub>2</sub>), 2.94 (septet, 2H, CHMe<sub>2</sub>), 1.70 (d, 6H, CHMe<sub>2</sub>), 1.46 (s, 6H, ArN(*Me*)CCHC(*Me*)NAr), 1.38 (d, 6H, CHMe<sub>2</sub>), 1.33 (d, 6H, CHMe<sub>2</sub>), 1.06 (d, 6H, CHMe<sub>2</sub>), -0.31 (s, 9H, Ti=CH-SiMe<sub>3</sub>). <sup>13</sup>C NMR (23 °C, 100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 320.1 (Ti=CHSiMe<sub>3</sub>, J<sub>C-H</sub> = 98 Hz), 167.8 (ArN(*Me*)CCHC(*Me*)NAr), 145.0 (C<sub>6</sub>H<sub>3</sub>), 142.8 (C<sub>6</sub>H<sub>3</sub>), 140.3 (C<sub>6</sub>H<sub>3</sub>), 124.6 (C<sub>6</sub>H<sub>3</sub>), 124.5 (C<sub>6</sub>H<sub>3</sub>), 96.07 (ArN(*Me*)CCHC(*Me*)NAr), 30.28 (CHMe<sub>2</sub>), 28.91 (CHMe<sub>2</sub>), 25.95 (*Me*), 24.69 (*Me*), 24.49 (*Me*), 24.39 (*Me*), 23.51 (*Me*), 0.69 (Ti=CH-SiMe<sub>3</sub>). <sup>19</sup>F NMR (23 °C, 282.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -77.86 (s, TiO<sub>3</sub>SCF<sub>3</sub>).

#### 2.5. Thermolysis of (*nacnac*)Ti=CHSiMe<sub>3</sub>(OTf) (2): synthesis of

##### [ArNC(*Me*)CHC(*Me*)=CHSiMe<sub>3</sub>]Ti=NAr(OTf) (3)

In a Schlenk flask was dissolved **2** [250 mg, 0.36 mmol] in 20 ml of benzene and the solution was heated to 60 °C for 70 min, upon which a benzene insoluble precipitate formed. Monitoring the reaction mixture revealed two products to form in a 3:1 ratio approximately. The mixture was filtered, dried under reduced pressure and extracted with hexane. Recrystallization from concentrated hexane solution afforded brown color crystals of **3** [major product, 165 mg, 0.24 mmol, 66% yield]. Attempts to isolate the second product were hampered by its high solubility in most common organic solvents. For **3**: <sup>1</sup>H NMR (23 °C,

399.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.09–6.80 (m, 6H, ArH), 5.06 (s, 1H, ArN(*Me*)CCHC(*Me*)NAr), 3.80 (septet, 2H, CHMe<sub>2</sub>), 2.01–2.11 (br, 5H, isopropyl methine and backbone *Me* resonances overlapped), 1.81 (s, 1H, HCSiMe<sub>3</sub>C(*Me*)CHC(*Me*)), 1.58 (s, 3H, ArN(*Me*)CCHC(*Me*)CH-SiMe<sub>3</sub>), 1.44 (d, 6H, CHMe<sub>2</sub>), 1.18 (d, 6H, CHMe<sub>2</sub>), 1.06 (d, 6H, CHMe<sub>2</sub>), 0.87 (d, 6H, CHMe<sub>2</sub>), 0.25 (s, 9H, CHSiMe<sub>3</sub>). <sup>13</sup>C NMR (23 °C, 100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ 168.3 (ArN(*Me*)CCHC(*Me*)), 158.7 (SiMe<sub>3</sub>CHC(*Me*)CHC(*Me*)), 145.4 (C<sub>6</sub>H<sub>3</sub>), 143.3 (SiMe<sub>3</sub>CHC(*Me*)CHC(*Me*)), 139.6 (C<sub>6</sub>H<sub>3</sub>), 125.5 (C<sub>6</sub>H<sub>3</sub>), 123.9 (C<sub>6</sub>H<sub>3</sub>), 123.8 (C<sub>6</sub>H<sub>3</sub>), 122.6 (br, CF<sub>3</sub>), 119.5 (C<sub>6</sub>H<sub>3</sub>), 100.7 (ArN(*Me*)CCHC(*Me*)CH-SiMe<sub>3</sub>), 31.97 (CHMe<sub>2</sub>), 29.56 (CHMe<sub>2</sub>), 28.43 (*Me*), 27.85 (*Me*), 24.81(*Me*), 24.32 (*Me*), 23.41 (*Me*), 14.35 (*Me*), 1.02 (CHSiMe<sub>3</sub>). <sup>19</sup>F NMR (23 °C, 282.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -75.78 (s, TiO<sub>3</sub>SCF<sub>3</sub>).

#### 2.6. X-ray crystallographic data

Crystal data for C<sub>37</sub>H<sub>63</sub>N<sub>2</sub>Si<sub>2</sub>Ti, **1**: *M* = 639.97, Monoclinic, space group *P*2(1)/*n*, *a* = 10.1486(5), *b* = 21.5396(10), *c* = 17.9677(9) Å, β = 91.2250(10)°, α = γ = 90°, *U* = 3926.8(3) Å<sup>3</sup> [3], *Z* = 4, *D*<sub>c</sub> = 1.083 g cm<sup>-3</sup>, μ(Mo Kα) = 0.304 mm<sup>-1</sup>, *T* = 138(2) K, Bruker SMART 6000, total reflections 169,258, unique reflections *F* > 4σ(*F*) 14,252, observed reflections 9426 (*R*<sub>int</sub> = 0.0780). The structure was solved using SHELXS-97 and refined with SHELXL-97. 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. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. GOF = 0.991 and the final refinement converged at *R*(*F*) = 0.0403 (observed data) and *wR*(*F*<sup>2</sup>) = 0.1136 (refinement data). Crystal data for C<sub>38</sub>H<sub>59</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>SSiTi, **2**-THF: *M* = 772.92, Orthorhombic, space group *Pbca*, *a* = 19.4455(14), *b* = 18.7889(13), *c* = 22.4337(16) Å, α = β = γ = 90°, *U* = 8196.4(10) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.253 g cm<sup>-3</sup>, μ(Mo Kα) = 0.342 mm<sup>-1</sup>, *T* = 136(2) K, Bruker SMART 6000, total reflections 117,790, unique reflections *F* > 4σ(*F*) 9427, observed reflections 5824 (*R*<sub>int</sub> = 0.0938). The structure was solved using SHELXS-97 and refined with SHELXL-97.2. 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. Many of the hydrogen atoms were visible in subsequent difference Fourier synthesis maps, and all hydrogens were included as either isotropically refined or in idealized riding positions. GOF = 1.033, and the final refinement converged at *R*(*F*) = 0.0612 (observed data) and *wR*(*F*<sup>2</sup>) = 0.1845 (refinement data).

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## Appendix A. Supplementary material

CCDC 628378 and 628379 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.033.

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