

Terminal Titanium(IV) (Trimethylsilyl)imides Prepared by Oxidatively Induced Trimethylsilyl Abstraction

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Summary: Titanium (trimethylsilyl)imide triflate complexes of the type $(L)Ti=NSiMe_3(OTf)$ ($L^- = [ArNC(CH_3)_2CH]$, $Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$; $L^- = N[2\text{-}P(CHMe_2)_2\text{-}4\text{-}MeC_6H_3]_2$) can be readily prepared by one-electron oxidation and subsequent trimethylsilyl abstraction in the Ti(III) precursors $(L)TiCl(N\{SiMe_3\}_2)$.

Early-transition-metal complexes containing the silylimide functionality $[NSiR_3]^{2-}$ are well-known.¹ In the context of group 4 transition metals, the silylimide is typically prepared by α -hydrogen abstraction,² silyl chloride elimination,^{3,4} and, more recently, transimination reactions.⁵ Other synthetic strategies to generate the $Ti=NSiR_3$ motif include oxidation reactions of low-valent metal species with N_3SiR_3 ^{6,7} or silyl-substituted benzamminates.⁸ In certain cases, polynuclear precursors such as $[Ti(NSiMe_3)Cl_2]_3$ ³ can be converted to the corresponding monomer via salt elimination reactions with sterically imposing ligands.⁹ Despite the silylimide ligand being a common theme in transition metals,¹ few examples of the terminal (trimethylsilyl)imide group exist for group 4 metals.^{4,6,7,9} In this paper we report a systematic approach to the terminal (trimethylsilyl)imide functionality on titanium(IV). The process involves a synthetic strategy combining a one-electron oxidation coupled with a trimethylsilyl abstraction step. Preparation of the silylimide product is quantitative by NMR spectroscopy and may be obtained in a highly pure form upon recrystallization. Most notably, this technique is versatile and can encompass both bis-

and tris-chelate ligands such as $[ArNC(CH_3)_2CH]$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$)¹⁰ and PNP^- ($N[2\text{-}P(CHMe_2)_2\text{-}4\text{-}MeC_6H_3]_2$).¹¹

Previously, our group reported that one-electron oxidation of titanium(III) bis-neopentyl- or bis-anilide (NHAr) promoted α -hydrogen abstraction to afford terminal titanium alkylidene¹² or arylimide¹³ complexes concurrent with alkane or aniline formation. Realizing that alkane and aniline are both byproducts generated in these types of reactions, we speculated whether other groups could be also eliminated in one-electron-oxidation processes. For this reason, we turned our attention to the hexamethylsilylazide group, since one would expect trimethylsilyl-X ($X^- = \text{halide, pseudohalide}$) elimination to be a thermodynamically favored process.

Accordingly, when a toluene solution of $([ArNC(CH_3)_2CH]TiCl_2(THF))^{12a}$ or $(PNP)TiCl_2^{12d}$ is treated with an equimolar amount of $NaN\{SiMe_3\}_2$, the complex $([ArNC(CH_3)_2CH]TiCl(N\{SiMe_3\}_2)$ (**1**) or $(PNP)TiCl(N\{SiMe_3\}_2)$ (**2**) is obtained in good to moderate yields (**1**, 85%; **2**, 64%) (Scheme 1).¹⁴ Solution magnetic moment measurements of **1** and **2** are consistent with a d^1 paramagnetic species (Evans method). The molecular structure of **1** displays a four-coordinate Ti(III) complex in a highly distorted tetrahedral environment.¹⁴ Salient features for the molecular structure of **1** include a titanium–amide distance of 1.961(2) Å with the silylamide N being essentially planar. To avoid clashes with the β -diketiminato aryl groups, one trimethylsilyl substituent is oriented away from the isopropyl aryl groups and NCCCNTi framework. This feature places one of the $SiMe_3$ amide groups in close proximity to the chloride ligand (~ 3.76 Å, Figure 1). The orientation of such a group implies that trimethylsilyl chloride elimination could be, in principle, a viable reaction. On the other hand, the molecular structure of **2** confirms a monomeric, five-coordinate bis-(trimethylsilyl)amide titanium complex supported by the pincer ligand PNP (Figure 1). Analogous to the molecular structure of complex **1**, one of the bis(trimethylsilyl)amide silyl groups in **2** is oriented syn to the chloride ligand, but the distance is significantly longer (~ 4.12 Å, Figure 1).¹⁴

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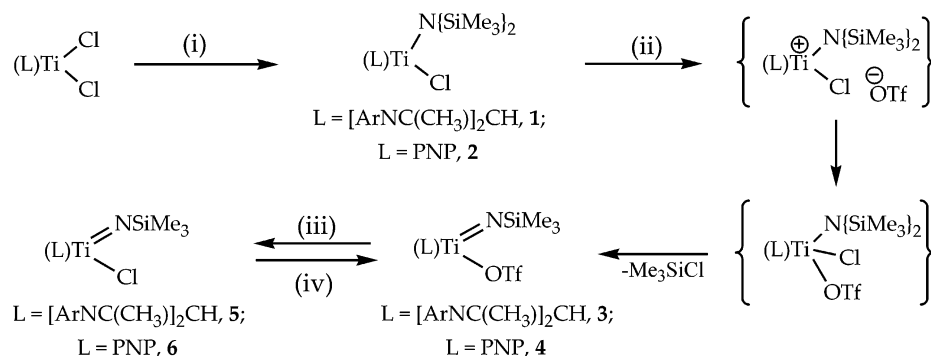
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Scheme 1. Synthesis of Complexes 1 and 2 and Subsequent Oxidation To Form 3 and 4^a

^a Complexes **3** and **4** can be converted into the Cl⁻ derivatives **5** and **6**, and subsequent Cl⁻ abstraction can regenerate the OTf⁻ derivatives. The compounds shown in brackets have not been observed spectroscopically. Legend: (i) NaN{SiMe₃}₂, -35 °C, toluene; (ii) [FeCp₂][OTf], -35 °C, THF; (iii) MgCl₂, THF; (iv) AgOTf, C₆D₆.

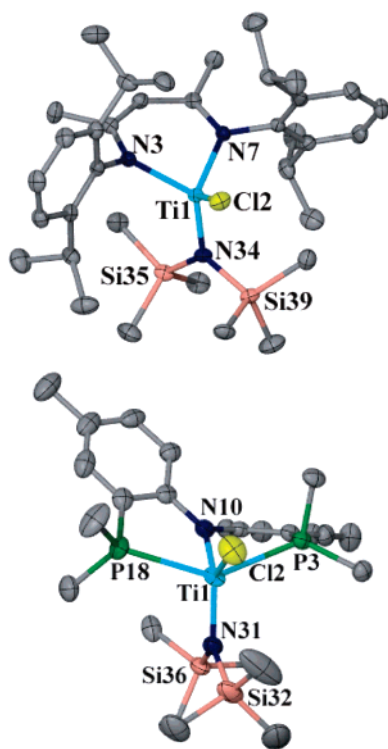


Figure 1. Molecular structures of complexes **1** (top) and **2** (bottom), with thermal ellipsoids at the 50% probability level. H atoms and ⁱPr methyls (**2**) have been omitted for clarity. Selected bond distances (reported in Å) and angles (reported in deg) are as follows. For **1**: Ti1–N34, 1.960(2); Ti1–N3, 2.051(2); Ti1–N7, 2.075(2); Ti1–Cl2, 2.2950(5); N34–Si35, 1.748(3); N34–Si39, 1.755(3); N3–Ti1–N7, 90.86(5). For **2**: Ti1–N31, 1.929(3); Ti1–N10, 2.057(2); Ti1–P3, 2.615(4); Ti1–P18, 2.690(2); Ti1–Cl2, 2.351(3); P3–Ti1–P18, 140.39(4).

In the absence of moisture and oxygen complexes **1** and **2** are indefinitely stable as a solid or in solution. However, when a THF solution of **1** or **2** is treated with 1 equiv of [FeCp₂][OTf], trimethylsilyl chloride, FeCp₂, and the silylimide ([ArNC(CH₃)₂CH)Ti=NSiMe₃(OTf) (**3**) or (PNP)Ti=NSiMe₃(OTf) (**4**) are formed quantitatively, as evidenced by ¹H NMR spectroscopy (Scheme 1). Separation of **3** or **4** from the FeCp₂ is easily achieved via recrystallization of the reaction mixture from pentane or Et₂O at -35 °C. Vacuum transfer of the volatiles from either reaction reveals only Me₃SiCl to be generated from the one-electron trimethylsilyl abstraction process, thus suggesting that Me₃SiCl formation is thermodynamically favored over Me₃SiOTf formation. We propose that compounds **3** and

4 occur via an outer-sphere one-electron oxidation to form FeCp₂ and the putative [(L)TiCl(N{SiMe₃}₂)]+[OTf]⁻ complexes, which smoothly undergo coordination of the triflate ligand to promote Me₃SiCl extrusion concurrent with Ti=NSiMe₃ linkage formation (Scheme 1).

The molecular structure of complex **3**¹⁴ shows a rare example² of a terminal and four-coordinate titanium (trimethylsilyl)imido complex with a short Ti(1)–N(33) bond length of 1.689(2) Å (Figure 2). Most notably, the Ti–N_{imido}–Si angle (164.8(6)°) is bent, which implies that a pseudo Ti=N–SiMe₃ bond may not be heavily involved in the bonding scheme for this system. Sterics, however, could also account for the deviation from linearity. In the molecular structure of **3**, the metal center deviates ~1.14 Å above the NCCCN plane (Figure 1), and the low-coordinate environment at the titanium center promotes weak interactions of the metal with both β-carbons of the NCCCN β-diketiminato ring (2.677(3) and 2.685(3) Å). Complex **3** is a close relative to four-coordinate titanium arylimide complexes reported previously.^{13,15}

The greater coordination environment in **4** prompted us to collect single-crystal X-ray diffraction data (Figure 2).¹⁴ As expected, the molecular structure of **4** reveals a five-coordinate titanium(IV) center containing a terminal (trimethylsilyl)imido ligand (Ti–N31 = 1.693(6) Å, Ti–N_{imido}–Si = 173.7(1)°). For comparison, the pincer–amide distance (Ti–N10 = 2.050(5) Å) is significantly longer than the imide linkage. As observed with **3**, deviation from linearity is also evident from the Ti–N–Si angle, and the PNP pincer framework displays “trans-like” phosphines (P–Ti–P = 144.70(2)°, Figure 2), with the PNP amide nitrogen being essentially planar. We propose that sp hybridization at the imide nitrogen in complex **4** might be enforced more by sterics^{12d} than an electronic argument. The poor quality of the X-ray data for **3**, however, forbids us from making any accurate comparisons with the structural features of **4**.

Conveniently, the triflate ligand in compounds **3** and **4** can be readily displaced with MgCl₂ in THF to afford the (trimethylsilyl)imide chlorides ([ArNC(CH₃)₂CH)Ti=NSiMe₃(Cl) (**5**) and (PNP)Ti=NSiMe₃(Cl) (**6**) quantitatively.¹⁴ Conversion of **5** and **6** back to **3** and **4**, respectively, can be achieved with addition of 1 equiv of AgOTf in C₆D₆ (Scheme 1).¹⁴ The NMR spectra of **5** and **6** were analogous to those of **3** and **4**, albeit in the absence of the ¹⁹F NMR resonance for the triflate group.¹⁴

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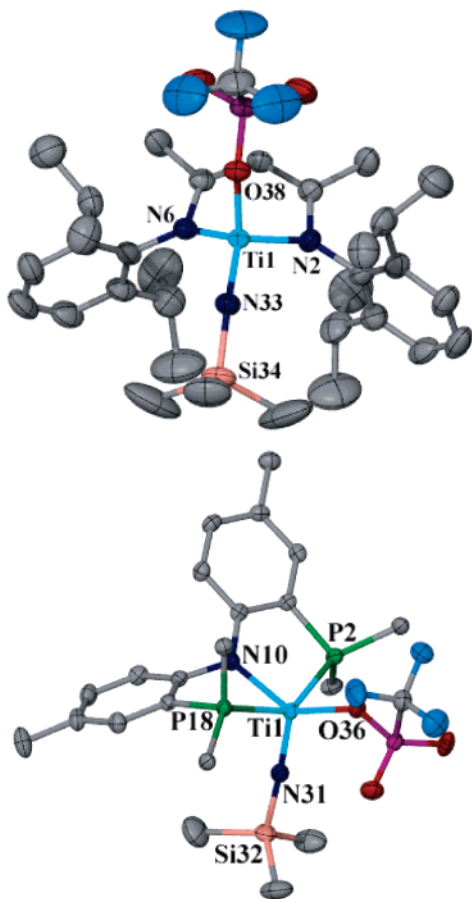


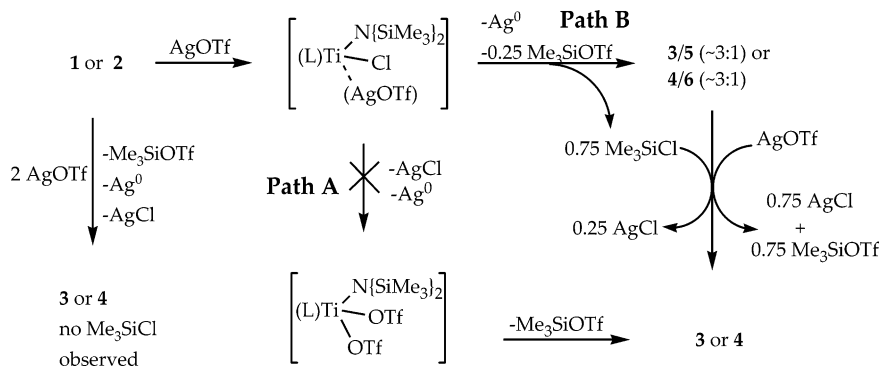
Figure 2. Molecular structures of complex **3** (top) and **4** (bottom), with thermal ellipsoids at the 50% probability level. H atoms and ⁱPr methyls (**4**) have been omitted for clarity. Selected bond distances (reported in Å) and angles (reported in deg) are as follows. For **3**: Ti1–N33, 1.689(2); Ti1–O38, 2.0235(18); Ti1–N2, 1.985(2); Ti1–N6, 1.980(2); N2–Ti1–N6, 95.50(9); Ti1–N33–Si34; 164.8(6). For **4**: Ti1–N31, 1.693(6); Ti1–N10, 2.050(5); Ti1–O36, 2.019(3); Ti1–P2, 2.6015(6); Ti1–P18, 2.5850(6); P2–Ti1–P18, 144.70(2); Ti1–N31–Si32, 173.7(1).

We wondered if other common oxidants could also promote trimethylsilyl abstraction. In view of that, when 1 equiv of AgOTf was added to **1** or **2** in toluene, a mixture of compounds **3/5** or **4/6** were observed spectroscopically by ¹H and ¹⁹F NMR (and ³¹P NMR in the case of **4/6**) in a 3:1 ratio. The observation that the solid of **3** or **4** was marred by the content of **5** or **6** implied that Me₃SiCl and Me₃SiOTf should be also generated

in the reaction mixture (Scheme 2). In fact, examination of the volatiles from the reaction confirmed the formation of Me₃SiCl and Me₃SiOTf in approximately a 3:1 ratio.¹⁶ For this reason, it appears that one-electron oxidation of **1** or **2** with AgOTf is partially discriminative for SiCl vs SiOTf bond formation, which could be attributed to AgOTf being an inner-sphere one-electron oxidant as opposed to [FeCp₂][OTf]. We believe that a transmetalation reaction between AgOTf and **1** does not precede the oxidation step, given the greater formation of Me₃SiCl vs Me₃SiOTf and the absence of Ti(III) byproducts. Independent experiments between **3** or **4** and Me₃SiCl show this process to be very slow, thus insinuating that triflate for chloride exchange is not a likely pathway.^{14,17} Despite the mixture of imide derivatives, our ability to convert **5** or **6** to the triflate analogue (vide infra) suggested that a second equivalent of AgOTf might promote anion exchange (Cl[−] for OTf[−]).

Gratifyingly, when complex **1** or **2** is treated instead with 2 equiv of AgOTf in toluene at −35 °C, trimethylsilyl abstraction cleanly and rapidly (~5 min) occurs to form **3** or **4**, respectively (76–80% isolated yield; Scheme 2).¹⁴ However, we were surprised to observe Me₃SiOTf as the *only volatile byproduct* from the reaction mixture (e.g., for the **1** → **3** conversion with 2 equiv of AgOTf). This result suggested that AgOTf might be not only oxidizing **1** to an intermediate such as “[ArNC(CH₃)₂CH]TiCl(OTf)(N{SiMe₃})₂” but also promoting Cl[−] for OTf[−] exchange to afford the putative “[ArNC(CH₃)₂CH]Ti(OTf)₂(N{SiMe₃})₂”. The latter complex would subsequently generate **3** and Me₃SiOTf, along with Ag⁰ and AgCl precipitates (pathway A, Scheme 2). Despite this possibility, and given our ability to generate a mixture of silylimides from the **1** → **3/5** conversion with 1 equiv of AgOTf (3:1 ratio; vide supra), we propose that a different pathway is involved. Hence, 1 equiv of AgOTf reacts with **1** or **2** to form a hypothetical “(L)TiCl(N{SiMe₃})₂(AgOTf)” adduct. This reactive intermediate rapidly expels Ag⁰ metal, which promotes trimethylsilyl abstraction to form the two silylimide derivatives. Subsequent Cl[−] for OTf[−] exchange with the second equivalent of AgOTf furnishes only the silylimide compound **3** or **4** (pathway B, Scheme 2). The absence of Me₃SiCl in the reaction mixture suggests that another exchange might be taking place. Evidence for Me₃SiCl consumption is provided by an independent reaction involving AgOTf and Me₃SiCl, which rapidly afforded Me₃SiOTf quantitatively along with a white precipitate (Scheme 2). As a result, these observations suggest that an intermediate such as “(L)TiCl(N{SiMe₃})₂(AgOTf)” leads to a mixture of silylimides (**3/5** or **4/6**, in approximately a 3:1 ratio),¹⁶ 1 equiv of Ag⁰, 0.25 equiv of Me₃SiOTf, and 0.75 equiv of Me₃SiCl. The second

Scheme 2. Synthesis of Complexes 3 and 4 from the Addition of 2 Equiv of AgOTf to 1 and 2, Respectively, and Proposed Mechanism^a



^a The reaction involving 1 equiv of AgOTf and **1** or **2** is also displayed. The ratios of Me₃SiCl and Me₃SiOTf are approximate values and have been standardized to 3:1, respectively.¹⁶

equivalent of AgOTf would then rapidly convert, in the appropriate ratios, Me₃SiCl into Me₃SiOTf and AgCl and **5** into **3** and AgCl (Scheme 2). Since these reactions are so rapid, anion exchange of the triflate derivative **3** or **4** with Me₃SiCl should not be a competing pathway (vide supra).

In conclusion, we have shown that one-electron oxidation of Ti(III) bis(trimethylsilyl)amide chloride complexes promotes trimethylsilyl abstraction to afford Ti(IV) systems bearing the terminal (trimethylsilyl)imide functionality. Discrepancies observed between the reagents [FeCp₂][OTf] and AgOTf manifest clearly the distinctions between outer-sphere and inner-sphere

(16) Conversion of **1** to **3** generated a 3:1 ratio of Me₃SiCl and Me₃-SiOTf, respectively, while the conversion of **2** to **4** generated the same byproducts in an approximately 5.7:1 ratio. For the purposes of clarity we generalize that Me₃SiCl and Me₃SiOTf are formed in approximately a 3:1 ratio.

(17) Addition of Me₃SiCl (~3 equiv) to **3** led only to 25% conversion to **5** after ~3 h.

one-electron oxidants. We are currently exploring the chemistry of these (trimethylsilyl)imide scaffolds.

Acknowledgment. This work is dedicated to the memory of Prof. Henry Taube, whose work has and will continue to inspire scientists studying electron transfer reactions. We thank Indiana University, the Dreyfus Foundation, the Sloan Foundation, and the NSF (Grant No. CHE-0348941) for financial support of this research. B.C.B. acknowledges the Lubrizol Foundation for a Graduate Fellowship.

Supporting Information Available: Text giving complete experimental details and spectroscopic and analytical data for complexes **1–6** and CIF files giving crystallographic data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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