

**Supporting Information for the Paper Entitled “Terminal
Titanium(IV) Trimethylsilylimides Prepared by
Oxidatively-Induced Trimethylsilyl Abstraction ”**

Brad C. Bailey, Falguni Basuli, John C. Huffman, and Daniel J. Mindiola*

*Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405 (USA)*

Experimental Section

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.¹ 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.² Diethylether was dried by passage through a column of activated alumina.² 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. C₆D₆ and C₇D₈ were purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. THF-*d*8 was purchased from CIL and used as received. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li([ArNC(Me)]₂CH)³ (Ar = 2,6-ⁱPr₂C₆H₃), ([ArNC(Me)]₂CH)TiCl₂(THF)⁴ and Li(PNP) (PNP = N[2-P(CHMe₂)₂-4-methylphenyl]₂)⁵ were prepared according to the literature. Ferrocenium trifluoromethanesulfonate was prepared by adding silver trifluoromethanesulfonate to a solution of ferrocene in CH₂Cl₂, then recrystallizing from a THF/CH₂Cl₂ mixture at -35 °C. All other chemical were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ¹H and ¹³C NMR are reported with reference to solvent resonances (residual C₆D₅H in C₆D₆, 7.16 ppm and 128.0 ppm). ¹⁹F NMR chemical shifts are reported with respect to external HOCOCF₃ (-78.5 ppm). ³¹P NMR chemical shifts are reported with respect to external H₃PO₄ (aqueous solution, δ 0.0 ppm).

Solution magnetization measurements were determined by the method of Evans.^{6,7} X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N₂ (g) at low temperatures.^{8,9}

Preparation of ([ArNC(Me)]₂CH)TiCl(N{SiMe₃})₂ (1)

In a round bottom flask was dissolved ([ArNC(Me)]₂CH)TiCl₂(THF) [550 mg, 0.90 mmol] in toluene (50 mL) and the solution was cooled to –35 °C. To the solution was added dropwise a cold (–35 °C) toluene (20 mL) solution of sodium bis(trimethylsilyl)amide [165.7 mg, 0.90 mmol]. After stirring for 3 hours the solution was dried in vacuo. The residue was dissolved in ether and filtered. The filtrate was reduced in volume and cooled to –35 °C to afford **1** as dark red blocks [508 mg, 0.77 mmol, 85% yield].

For **1**: ¹H NMR (C₆D₆, 300.1 MHz, 25 °C): δ 8.77 (Δv_{1/2} = 46 Hz), 6.55 (Δv_{1/2} = 34 Hz), 4.86 (Δv_{1/2} = 40 Hz), 4.13 (Δv_{1/2} = 87 Hz), 2.95 (Δv_{1/2} = 44 Hz), 2.11 (Δv_{1/2} = 152 Hz), 0.88 (Δv_{1/2} = 593 Hz). Evans Magnetic Moment (C₆D₆, 298K): μ_{eff} = 1.93μ_B. Anal. Calcd. for C₃₅H₅₉N₃Si₂ClTi : C, 63.56; H, 8.99; N, 6.35. Found: C, 63.26; H, 8.68; N, 6.32.

Preparation of (PNP)TiCl(N{SiMe₃})₂ (2)

In a 125 mL Erlenmeyer flask was added TiCl₃(THF)₃ [485 mg, 1.309 mmol] to toluene (20 mL) and the solution was cooled to –35 °C. To the green-blue solution was added a cold (–35 °C) yellow toluene (20 mL) solution of Li(PNP) [560 mg, 1.286 mmol]. The solution changed from blue-green to red then finally to a purple color. The solution was

stirred for 1 hour and then cooled to $-35\text{ }^{\circ}\text{C}$. Upon cooling, sodium bis(trimethylsilyl)amide [252 mg, 1.374 mmol] diluted in toluene (10 mL) was added dropwise. The solution changed from purple to brown-red and was stirred for 2 hours. The solution was then dried in vacuo and redissolved in pentane. The solution was filtered through a bed of celite and the resulting yellow-brown solution was reduced in volume under vacuo, and cooled to $-35\text{ }^{\circ}\text{C}$ to yield **2** as green blocks [560 mg, 0.833 mmol, 64% yield].

For **2**: ^1H NMR ($23\text{ }^{\circ}\text{C}$, 399.8 MHz, C_6D_6): δ 7.59 ($\nu_{1/2} = 17\text{ Hz}$), 7.05 ($\nu_{1/2} = 12\text{ Hz}$), 7.04 ($\nu_{1/2} = 12\text{ Hz}$), 7.00 ($\nu_{1/2} = 17\text{ Hz}$), 6.97 ($\nu_{1/2} = 35\text{ Hz}$), 5.95 ($\nu_{1/2} = 179\text{ Hz}$), 3.37 ($\nu_{1/2} = 14\text{ Hz}$), 2.31 ($\nu_{1/2} = 5\text{ Hz}$), 2.03 ($\nu_{1/2} = 43\text{ Hz}$), 1.10 ($\nu_{1/2} = 37\text{ Hz}$), 0.12 ($\nu_{1/2} = 3\text{ Hz}$). $\mu_{\text{eff}} = 1.64\text{ }\mu\text{B}$ (C_6D_6 , 298 K, Evans' method). Anal. Calcd. for $\text{C}_{32}\text{H}_{58}\text{N}_2\text{SiP}_2\text{TiCl}$: C, 57.17; H, 8.70; N, 4.17. Found: C, 56.88; H, 8.81; N, 4.11.

Preparation of $([\text{ArNC}(\text{Me})]_2\text{CH})\text{Ti}=\text{NSiMe}_3(\text{OTf})$ (**3**)

Using $[\text{FeCp}_2][\text{OTf}]$: In a vial was dissolved **1** [127 mg, 0.19 mmol] in THF (10 mL) and the solution was cooled to $-35\text{ }^{\circ}\text{C}$. To the cold dark solution was added solid $[\text{FeCp}_2][\text{OTf}]$ [68 mg, 0.19 mmol]. The color of the solution rapidly changed to pale yellow ($\sim 3\text{-}5\text{ min}$). The solution was then stirred for 1 hour and dried under vacuum. The residue was extracted with pentane and filtered. The filtrate was reduced in volume under reduced pressure, and then cooled to $-35\text{ }^{\circ}\text{C}$. After 5 min white crystals of **3** [72 mg, 0.10 mmol, 53% yield] were collected. Further cooling of the decanted liquid afforded a mixture of FeCp_2 and compound **3**. Formation of FeCp_2 and **3** is quantitative when the crude reaction is examined by ^1H NMR spectroscopy.

Using **AgOTf**: In a vial was dissolved **1** [167 mg, 0.25 mmol] in toluene (10 mL) and the solution was cooled to $-35\text{ }^{\circ}\text{C}$. To the cold solution was added solid AgOTf [132.7 mg, 0.51 mmol], and the color of the solution changed to light yellow with copious amounts of precipitate. The solution was stirred for 2 hours, filtered and then dried in vacuo. The residue was extracted with Et₂O and filtered. The filtrate was reduced in volume in vacuo, and cooled to $-35\text{ }^{\circ}\text{C}$ to afford **3** as colorless crystals [143 mg, 0.20 mmol, 80% yield]. The crude ¹H NMR spectrum of the reaction mixture reveals the conversion of **1**→**3** to be quantitative. When the same above reaction was done in C₆D₆ and analysis of volatiles indicated the presence of only Me₃SiOTf.

For **3**: ¹H NMR (23 $^{\circ}\text{C}$, 399.8 MHz, C₆D₆): δ 7.21-7.10 (m, 6H, Ar-*H*), 4.92 (s, 1H, ArN(Me)CCHC(Me)NAr), 3.14 (septet, 2H, CHMe₂), 3.95 (septet, 2H, CHMe₂), 1.74 (d, 6H, CHMe₂), 1.53 (s, 6H, ArN(*Me*)CCHC(*Me*)NAr), 1.39 (d, 6H, CHMe₂), 1.33 (d, 6H, CHMe₂), 0.95 (d, 6H, CHMe₂), -0.42 (s, 9H, Ti=N-SiMe₃). ¹³C NMR (23 $^{\circ}\text{C}$, 100.6 MHz, C₆D₆): δ 168.4 (ArN(Me)CCHC(Me)NAr), 144.8 (C₆H₃), 142.6 (C₆H₃), 140.2 (C₆H₃), 124.6 (C₆H₃), 124.1 (C₆H₃), 94.12 (ArN(Me)CCHC(Me)NAr), 29.91 (CHMe₂), 28.65 (CHMe₂), 25.85 (ArN(*Me*)CCHC(*Me*)NAr), 24.48 (*Me*), 24.22 (*Me*), 24.19 (*Me*), 23.52 (*Me*), 0.91 (Ti=N-SiMe₃). ¹⁹F NMR (23 $^{\circ}\text{C}$, 282.3 MHz, C₆D₆): δ -77.97 (s, Ti-O₃SCF₃). Anal. Calcd. for C₃₃H₅₀N₃SiO₃SF₃Ti : C, 56.48; H, 7.18; N, 5.98. Found: C, 56.64; H, 7.15; N, 5.82.

Preparation of (PNP)Ti=NTMS(OTf) (**4**)

Using **AgOTf**: In a vial was dissolved **2** [374 mg, 0.556 mmol] in toluene (7 mL) and the solution was cooled to $-35\text{ }^{\circ}\text{C}$. To the cold green solution was added solid AgOTf

[290 mg, 1.128 mmol]. The solution turned dark red with copious amounts of precipitate. The solution was stirred for 1 hour, dried in vacuo, and the residue was extracted with pentane and filtered. The dark red filtrate was reduced in volume in vacuo, and then cooled to $-35\text{ }^{\circ}\text{C}$ to afford **4** as red blocks [302 mg, 0.424 mmol, 76% yield].

Using **[FeCp₂][OTf]**: In a vial was dissolved **2** [78 mg, 0.116 mmol] in THF (5 mL) and the solution was cooled to $-35\text{ }^{\circ}\text{C}$. To the cold green solution was added solid **[FeCp₂][OTf]** [39 mg, 0.116 mmol]. The solution rapidly turned dark red, and was allowed to stir for 1 hour, and then dried in vacuo. The residue was extracted with Et₂O filtered. The dark red filtrate was reduced in volume under vacuo, and then cooled to $-35\text{ }^{\circ}\text{C}$. The solution was carefully decanted from yellow crystals of ferrocene, and reduced again in volume under vacuo to afford **4** as red blocks [58 mg, 0.081 mmol, 70% yield].

For **4**: ¹H NMR (23 $^{\circ}\text{C}$, 399.8 MHz, C₆D₆): δ 7.21 (dd, 1H, C₆H₃), 6.91 (d, 1H, C₆H₃), 6.85 (d, 1H, C₆H₃), 6.78 (m, 2H, C₆H₃), 6.72 (d, 1H, C₆H₃), 2.42 (sept, 1H, CHMe₂), 2.15-2.31 (m, 2H, CHMe₂), 2.12 (s, 3H, C₆H₃-Me), 2.06 (s, 3H, C₆H₃-Me), 1.95-2.09 (m, 1H, CHMe₂), 1.31-1.59 (m, 12H, CHMe₂), 1.05 (dd, 3H, CHMe₂), 0.95 (dd, 3H, CHMe₂), 0.72-0.80 (m, 6H, CHMe₂), 0.03 (s, 9H, Ti=N-SiMe₃). ¹³C NMR (23 $^{\circ}\text{C}$, 100.6 MHz, C₆D₆): δ 160.6 (d, C₆H₃), 157.4 (dd, C₆H₃), 133.5 (C₆H₃), 133.1 (C₆H₃), 132.9 (C₆H₃), 131.9 (d, C₆H₃), 131.7 (C₆H₃), 122.8 (C₆H₃), 120.6 (d, C₆H₃), 120.3 (d, C₆H₃), 116.1 (d, C₆H₃), 115.6 (d, C₆H₃), 24.5 (d, CHMe₂), 23.7 (d, CHMe₂), 20.9 (C₆H₃-Me), 20.4 (C₆H₃-Me), 20.4 (d, CHMe₂), 20.3 (d, CHMe₂), 20.0 (d, CHMe₂), 19.8 (d, CHMe₂), 19.5 (d, CHMe₂), 18.4 (d, CHMe₂), 17.5 (d, CHMe₂), 17.4 (d, CHMe₂), 17.0 (d, CHMe₂), 15.9 (d, CHMe₂), 2.7 (Ti=N-SiMe₃). ³¹P NMR (23 $^{\circ}\text{C}$, 121.5 MHz, C₆D₆): δ 28.4 (d, $J_{\text{P-P}} = 60$ Hz), 20.3 (d, $J_{\text{P-P}} = 60$ Hz). ¹⁹F NMR (23 $^{\circ}\text{C}$, 282.3 MHz, C₆D₆): δ -76.9 (Ti-OSO₂CF₃).

Anal. Calcd. for $C_{30}H_{49}N_2SiP_2TiO_3SF_3$: C, 50.56; H, 6.93; N, 3.93. Found: C, 50.31; H, 7.11; N, 3.79.

Preparation of $([ArNC(Me)]_2CH)Ti=NSiMe_3(Cl)$ (**5**)

In a vial was dissolved **3** [362 mg, 0.51 mmol] in THF (10 mL) and to the room temperature solution was added excess solid $MgCl_2$ [147.3 mg, 1.54 mmol]. The solution was stirred for 3 hours, and dried in vacuo. The solid was extracted with pentane, filtered through a bed of celite, and the filtrate reduced in volume under vacuo to afford colorless crystals of **5** [258 mg, 0.44 mmol, 86% yield] (the crude NMR shows the conversion of **3**→**5** to be quantitative).

For **5**: 1H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.21-7.10 (m, 6H, Ar-*H*), 4.86 (s, 1H, ArN(Me)CCHC(Me)NAr), 3.48 (septet, 2H, CHMe₂), 3.31 (septet, 2H, CHMe₂), 1.70 (d, 6H, CHMe₂), 1.50 (s, 6H, ArN(Me)CCHC(Me)NAr), 1.42 (d, 6H, CHMe₂), 1.22 (d, 6H, CHMe₂), 1.03 (d, 6H, CHMe₂), -0.27 (s, 9H, Ti=N-SiMe₃). ^{13}C NMR (23°C, 100.6 MHz, C_6D_6): δ 168.5 (ArN(Me)CCHC(Me)NAr), 144.7 (C_6H_3), 142.7 (C_6H_3), 140.9 (C_6H_3), 127.4 (C_6H_3), 124.5 (C_6H_3), 124.1 (C_6H_3), 95.69 (ArN(Me)CCHC(Me)NAr), 29.06 (CHMe₂), 28.69 (CHMe₂), 26.99 (ArN(Me)CCHC(Me)NAr), 24.46 (Me), 24.36 (Me), 23.98 (Me), 23.69 (Me), 1.35 (Ti=N-SiMe₃). Anal. Calcd. for $C_{32}H_{50}N_3SiClTi$: C, 65.35; H, 8.56; N, 7.14. Found: C, 65.00; H, 8.30; N, 6.89.

Preparation of (PNP)Ti=NSiMe₃(Cl) (**6**)

In a vial was dissolved **4** [66 mg, 0.093 mmol] in THF (6 mL) and to the room temperature solution was added excess solid $MgCl_2$ [26 mg, 0.273 mmol]. The solution

was stirred for 3 hours, and then dried in vacuo. The dark red solution was extracted with pentane, filtered through a bed of celite, and then reduced in volume under vacuo to afford dark red crystals of **6** [46 mg, 0.077 mmol, 83% yield]. The crude ^1H NMR of the reaction mixture shows the conversion of **4**→**6** to be quantitative.

For **6**: ^1H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.27 (dd, 1H, C_6H_3), 6.93 (dd, 1H, C_6H_3), 6.85-6.88 (m, 2H, C_6H_3), 6.78-6.80 (m, 2H, C_6H_3), 2.46 (sept, 1H, CHMe_2), 2.16-2.29 (m, 2H, CHMe_2), 2.13 (s, 3H, $\text{C}_6\text{H}_3\text{-Me}$), 2.09 (s, 3H, $\text{C}_6\text{H}_3\text{-Me}$), 1.94 (sept, 1H, CHMe_2), 1.67 (dd, 3H, CHMe_2), 1.46 (dd, 3H, CHMe_2), 1.32-1.40 (m, 6H, CHMe_2), 1.25 (dd, 3H, CHMe_2), 0.94-1.02 (m, 6H, CHMe_2), 0.85 (dd, 3H, CHMe_2), 0.18 (s, 9H, Ti=N-SiMe_3). ^{13}C NMR (23 °C, 100.6 MHz, C_6D_6): δ 161.3 (d, C_6H_3), 159.3 (dd, C_6H_3), 133.1 (C_6H_3), 133.0 (C_6H_3), 132.9 (C_6H_3), 132.0 (C_6H_3), 130.0 (d, C_6H_3), 126.6 (d, C_6H_3), 120.5 (d, C_6H_3), 120.2 (d, C_6H_3), 116.5 (d, C_6H_3), 115.9 (d, C_6H_3), 24.7 (d, CHMe_2), 23.9 (d, CHMe_2), 20.9 ($\text{C}_6\text{H}_3\text{-Me}$), 20.5 ($\text{C}_6\text{H}_3\text{-Me}$), 20.4 (d, CHMe_2), 20.0 (d, CHMe_2), 19.9 (d, CHMe_2), 19.8 (d, CHMe_2), 19.6 (d, CHMe_2), 18.9 (d, CHMe_2), 18.2 (d, CHMe_2), 17.7 (d, CHMe_2), 17.0 (d, CHMe_2), 15.7 (d, CHMe_2), 3.2 (Ti=N-SiMe_3). ^{31}P NMR (23 °C, 121.5 MHz, C_6D_6): δ 29.0 (d, $J_{\text{P-P}} = 62$ Hz), 20.7 (d, $J_{\text{P-P}} = 62$ Hz). Anal. Calcd. for $\text{C}_{29}\text{H}_{49}\text{N}_2\text{SiP}_2\text{TiCl}$: C, 58.14; H, 8.24; N, 4.67. Found: C, 57.86; H, 8.50; N, 4.30.

Reaction of Complex **5** with 1 equiv of AgOTf to Prepare Complex **3**

In a vial was mixed **5** [35 mg, 0.06 mmol] and AgOTf [15.3 mg, 0.06 mmol]. To the solids was added C_6D_6 (1 mL) and reaction was allowed to stir for 2 hours. The solution was filtered, and ^1H and ^{19}F NMR spectrum of the filtrate indicated the complete conversion of **5** to **3**.

Reaction of Complex 1 with 1 equiv of AgOTf

In a vial was mixed **1** [55 mg, 0.08 mmol] and AgOTf [21.4 mg, 0.08 mmol]. To the solids was added C₆D₆ (1 mL) and the mixture stirred for 1 hr. The solution was filtered and ¹H NMR spectrum of the filtrate indicated the formation of **5**, **3**, Me₃SiOTf, and Me₃SiCl (1:3:1:3 ratio, respectively). The ¹⁹F NMR spectrum also suggested the presence of both **3** and Me₃SiOTf.

Reaction of 3 with TMS-Cl

In a vial was mixed complex **3** [35 mg, 0.05 mmol] and Me₃SiCl [15.4 mg, 0.14 mmol]. To the mixture was added C₆D₆ (1 mL) and the reaction allowed to stir for 3 hours. The ¹H and ¹⁹F NMR spectrum of the mixture indicated the presence of both **5** and **3** (1:3 ratio).

Reaction of 2 with 1 equiv of AgOTf

In a vial **2** [42 mg, 0.062 mmol] and AgOTf [16 mg, 0.062 mmol] were mixed. To the mixture was added C₆D₆ (1 mL) and the reaction was allowed to stir for 1 hour. The mixture was filtered, and ¹H NMR spectrum of the crude filtrate indicated the formation of **6**, **4**, Me₃SiOTf and Me₃SiCl (1:3:1:3 ratio, respectively). The ¹⁹F NMR spectrum also indicated the presence of both **4** and Me₃SiOTf.

Reaction of TMS-Cl with AgOTf

In a vial was mixed Me₃SiCl [60 mg, 0.55 mmol] and AgOTf [143 mg, 0.56 mmol]. To the mixture was added C₆D₆ (1 mL) to for a white precipitate. The reaction mixture was allowed to stir for 2 hours. The crude solution was filtered and ¹H and ¹⁹F NMR spectrum of the filtrate indicated the complete conversion of Me₃SiCl to Me₃SiOTf.

For **TMS-OTf**: ¹H NMR (23 °C, 399.8 MHz, C₆D₆): δ –0.001 (s). ¹⁹F NMR (23 °C, 282.3 MHz, C₆D₆): δ –77.87 (s).

References

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