Novel Volatile Azatranes of Group 4 Metals

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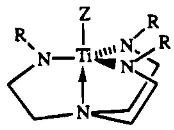
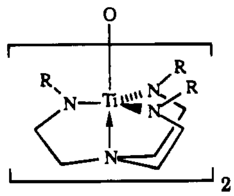
New azametallatranes of the type $\overline{Me_2NM(RNCH_2CH_2)_3N}$, where R = *i*-Pr, M = Ti (**16**), Zr (**17**), and Hf (**18**); R = $SiMe_3$, M = Ti (**19**), Zr (**20**), and Hf (**21**); and R = $SiMe_2$(*t*-Bu), M = Zr (**23**) and Hf (**24**), were prepared by metathesis reactions in moderate to high yield. During the course of the preparation of **19**, $Me_3SiO\overline{Ti(Me_3SiNCH_2CH_2)_3N}$, **25**, was formed in trace amounts. The latter compound was also synthesized by a metathesis reaction in a quantitative yield. Compounds **21** and **25** were structurally characterized and both were shown to exhibit a distorted trigonal bipyramidal metal center. Crystal data: **21**, orthorhombic, space group $P2_12_12_1$, a = 11.837(2) Å, b = 14.284(3) Å, c = 15.750(4) Å, V = 2662.9(9) Å^3, Z = 4, R = 0.0352; **25**, orthorhombic, space group $Pna2_1$, a = 21.772(2) Å, b = 11.481(4) Å, c = 11.566(1) Å, V = 2891(1) Å^3, Z = 4, R = 0.0341.

Introduction

Although the syntheses of tetrakis(dialkylamido)titanium,[1] -zirconium,[1] and -hafnium[2] compounds were reported three decades ago, the use of tren derivatives for this purpose has been described only recently.[3,4] In the latter reports the azatitanatranes **1**−**15** were characterized, of which **1** and **2** were reported from our laboratories.

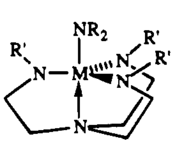


	Z	R
1[3]	NMe_2	Me
2[3]	O-*t*-Bu	Me
3[4a]	Cl	$SiMe_3$
4[4a]	*n*-Bu	$SiMe_3$
5[4a]	*s*-Bu	$SiMe_3$
6[4b]	Cl	$SiMe_2$(*t*-Bu)
7[4b]	-	$SiMe_2$(*t*-Bu)
8[4c]	Cl	Me
9[4c]	Cl	Et
10[4c]	Cl	*i*-Pr
11[4c]	OSO_2CF_3	Et
12[4c]	OSO_2CF_3	*i*-Pr
13[4c]	O_2CCH_3	Et



	R
14[4c]	Et
15[4c]	*i*-Pr

Our interest in preparing metal nitrides of Group 4 by MOCVD processes led us to investigate the possibility of preparing volatile (dialkylamino)azametallatranes of type **A**,



A

	M	R	R'
16	Ti	Me	*i*-Pr
17	Zr	Me	*i*-Pr
18	Hf	Me	*i*-Pr
19	Ti	Me	$SiMe_3$
20	Zr	Me	$SiMe_3$
21	Hf	Me	$SiMe_3$
22	Ti	Me	$SiMe_2$(*t*-Bu)
23	Zr	Me	$SiMe_2$(*t*-Bu)
24	Hf	Me	$SiMe_2$(*t*-Bu)

where M = Ti, Zr, or Hf, R = alkyl and R′ = alkyl or silyl. The nitrides of these metals have several important industrial applications. For example, TiN and ZrN can be used as wear-resistant coatings on machine tools,[5] gold substitutes for decorative coatings,[6] reflectance and hardness coatings for microelectronic devices,[7] diffusion barriers in various semiconductor metallization schemes,[8] and ceramics with high thermal impact resistance.[9] Nitrides of group 4 have also been investigated for their ability to catalyze hydrogen oxidation.[10]

Herein we report the syntheses and characterization of volatile precursors **16**−**21**, **23**, and **24**, as well as the crystal structures

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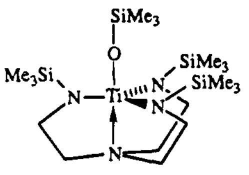
of **21** and **25** (which was obtained as a reaction product of **19** and adventitious water).



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Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified argon or nitrogen using standard Schlenk or drybox techniques.[11] All solvents were distilled from Na/benzophenone except acetonitrile which was distilled from P_4O_{10} under nitrogen. Sodium trimethylsilanolate (97%) was purchased from Aldrich and was used as received. $TiCl_4(THF)_2$, $ZrCl_4(THF)_2$, and $HfCl_4(THF)_2$ were synthesized according to literature procedures.[12] $Ti(NMe_2)_4$,[1] $Zr(NMe_2)_4$[1] and $Hf(NMe_2)_4$[2] were prepared by modified literature procedures in which $MCl_4(THF)_2$ (M = Ti, Zr, and Hf) was used instead of MCl_4. Tren derivatives $N(CH_2CH_2NHR)_3$ (where R = *i*-Pr[13] (*i*-Pr_3-tren), $SiMe_3$[14] (tms$_3$-tren) and $SiMe_2$(*t*-Bu) ((*t*-$BuMe_2Si)_3$-tren))[14] and $N(CH_2CH_2NLiR)_3$ (where R = $SiMe_3$[4a] and $SiMe_2$(*t*-Bu)[4b]) were synthesized using literature methods as were the azatitanatranes **3**[4a] and **6**.[4b]

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Nicolet NT300 or a Varian VXR 300 spectrometer in C_6D_6, using the protio impurity of the solvent as an internal reference for ^{1}H spectra, the ^{13}C resonance of the C_6D_6 as a reference for ^{13}C NMR spectra, and TMS in benzene as an external reference for ^{29}Si NMR spectra. Mass spectra were obtained on a Finnigan 4000 instrument or a Kratos MS-50 spectrometer. Melting points were determined with a Thomas-Hoover capillary apparatus. Elemental analyses were performed by Desert Analytics.

(Dimethylamino)triisopropylazatitanatrane, 16. A solution of $Ti(NMe_2)_4$ (1.75 g, 7.81 mmol) in 15 mL of toluene was added to a stirred solution of *i*-Pr_3-tren (2.11 g, 7.73 mmol) in 10 mL of toluene at room temperature. The reaction mixture was refluxed for 58 h. The initially yellow solution turned red, and dimethylamine was evolved. The solvent was removed *in vacuo* and the crude product was vacuum distilled (95−100 °C at 0.12 mmHg) to give 0.97 g (35% yield) of a red oil, which solidified upon standing for several hours. Further purification for characterizational purposes was achieved by recrystallization from acetonitrile in a freezer at about −30 °C; mp: 60−61 °C. No satisfactory elemental analysis results were obtained because of its extremely air- and moisture-sensitive nature. ^{1}H NMR: δ 4.42 (sept, 3 H, $^{3}J_{HH}$ = 6.6 Hz, CH), 3.21 (s, 6 H, $N(CH_3)_2$), 3.16 (t, 6 H, $^{3}J_{HH}$ = 6.0 Hz, *i*-$PrNCH_2$), 2.54 (t, 6 H, $^{3}J_{HH}$ = 6.0 Hz, $N(CH_2)_3$), 1.19 (d, 18 H, $^{3}J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$NMR: δ 53.66 ($N(CH_2)_3$), 52.84 (CH), 45.90 (*i*-$PrNCH_2$), 43.72 ($N(CH_3)_2$), 22.87 ($CH(CH_3)_2$). MS (EI), *m/z* (ion, relative intensity): 361 (M^+, 32), 346 ($M^+ - CH_3$, 12), 316 ($M^+ - HNMe_2$, 100).

(Dimethylamino)triisopropylazazirconatrane, 17. To a solution of 2.98 g (11.1 mmol) of $Zr(NMe_2)_4$ in 40 mL of dry, degassed THF, cooled to 0 °C, were added 3.10 g (11.4 mmol) of *i*-Pr_3-tren and a catalytic amount of $(NH_4)_2SO_4$. After the reaction mixture was stirred for 1 h at room temperature, it was refluxed for an additional 6 h, and then the solvent was removed under vacuum. The pure product, obtained by distillation at 110 °C, 20 mTorr, solidified upon standing for a few hours. Yield: 89%. Mp: 41−43 °C. ^{1}H NMR: δ 4.05 (sept, 3 H, $^{3}J_{HH}$ = 6.6 Hz, CH), 3.09 (t, 6 H, $^{3}J_{HH}$ = 5.7 Hz, *i*-$PrNCH_2$), 3.03 (s, 6 H, $N(CH_3)_2$), 2.53 (t, 6 H, $^{3}J_{HH}$ = 5.7 Hz, $N(CH_2)_3$), 1.21 (d, 18 H, $^{3}J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR: δ 52.50 ($N(CH_2)_3$), 49.43 (CH), 44.75 (*i*-$PrNCH_2$), 41.35 ($N(CH_3)_2$), 22.26 ($CH(CH_3)_2$). MS (EI), *m/z* (ion, relative intensity): 405 (M^+, 36), 362 (M^+ − *i*-Pr, 13), 361 ($M^+ - NMe_2$, 8). Anal. Calcd for $C_{17}H_{39}N_5Zr$: C, 50.45; H, 9.71. Found: C, 49.61; H, 9.73.

(Dimethylamino)triisopropylazahafnatrane, 18. The procedure was the same as that for **17** except that $Hf(NMe_2)_4$ was used instead of $Zr(NMe_2)_4$. Yield: 45%. Mp: 45−47 °C. ^{1}H NMR: δ 4.00 (sept, 3 H, $^{3}J_{HH}$ = 6.6 Hz, CH), 3.17 (t, 6 H, $^{3}J_{HH}$ = 5.7 Hz, *i*-$PrNCH_2$), 3.07 (s, 6 H, $N(CH_3)_2$), 2.44 (t, 6 H, $^{3}J_{HH}$ = 5.7 Hz, $N(CH_2)_3$), 1.22 (d, 18 H, $^{3}J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR: δ 52.46 ($N(CH_2)_3$), 49.22 (CH), 44.81 (*i*-$PrNCH_2$), 41.16 ($N(CH_3)_2$), 22.31 ($CH(CH_3)_2$). MS (EI), *m/z* (ion, relative intensity): 492 (M^+, 2), 449 (M^+ − *i*-Pr, 1), 448 ($M^+ - NMe_2$, 3).

(Dimethylamino)tris(trimethylsilyl)azatitanatrane, 19. Method A. A Schlenk flask was charged with 0.89 g (2.0 mmol) of **3** and 0.11 g (2.1 mmol) of $LiNMe_2$. After the flask was cooled to 0 °C, 30 mL of toluene was added. After the mixture was stirred at room temperature for 30 min, the reaction mixture was refluxed for 4 days and filtered through a pad of Celite. The volatile components in the filtrate were removed *in vacuo* to give a yellow-orange oil, from which a very small amount of crystals of **25** (20 mg) was isolated upon standing for 1 day. The remaining product (**19**, 90% yield) solidified upon standing after a few days. The presence of trace amounts of unknown impurities in this product was observed by its ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Attempts to obtain pure **19** by distillation or recrystallization have not been successful thus far. ^{1}H NMR: δ 3.31 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $SiNCH_2$), 3.29 (s, 6 H, $N(CH_3)_2$), 2.39 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $N(CH_2)_3$), 0.24 (s, 27 H, $SiCH_3$). $^{13}C\{^{1}H\}$ NMR: δ 63.27 ($N(CH_2)_3$), 49.32 ($SiNCH_2$), 48.40 ($N(CH_3)_2$), 2.38 ($SiCH_3$). $^{29}Si\{^{1}H\}$ NMR: δ 2.58. CIMS (NH_3, positive ion detection), *m/z* (ion, relative intensity): 452 (M^+ + H, 13), 407 ($M^+ - NMe_2$, 12), 363 ($(Me_3SiNHCH_2CH_2)_3N^+$ + H, 100). MS (EI), *m/z* (ion, relative intensity): 407 ($M^+ - NMe_2$, 4), 73 ($(CH_3)_3Si^+$, 100).

Method B. A solution of $Ti(NMe_2)_4$ (1.07 g, 4.75 mmol) in 15 mL of toluene was added to a stirred solution of tms$_3$-tren (1.69 g, 4.65 mmol) at room temperature. The reaction mixture was refluxed for 4 days, and the volatile components were removed *in vacuo* to give a red oil. A ^{1}H NMR spectrum of the crude product showed the presence of small amount of **19** and some unknown impurities. Attempts to isolate **19** from the mixture by distillation were not successful.

(Dimethylamino)tris(trimethylsilyl)azazirconatrane, 20. The procedure was the same as that for **17** except that tms$_3$-tren was used instead of *i*-Pr_3-tren. Yield, 74%. Mp: 62−63 °C. ^{1}H NMR: δ 3.21 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $SiNCH_2$), 3.02 (s, 6 H, $N(CH_3)_2$), 2.31 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $N(CH_2)_3$), 0.24 (s, 27 H, $SiCH_3$). $^{13}C\{^{1}H\}$ NMR: δ 62.97 ($N(CH_2)_3$), 46.58 ($SiNCH_2$), 43.66 ($N(CH_3)_2$), 1.72 ($SiCH_3$). $^{29}Si\{^{1}H\}$ NMR: δ 1.87. MS (EI), *m/z* (ion, relative intensity): 494 (M^+, 5), 450 ($M^+ - NMe_2$, 65), 449 ($M^+ - HNMe_2$, 100). CIMS (NH_3, positive ion detection), m/z (ion, relative intensity): 495 (M^+ + H, 19), 451 ($M^+ - NMe_2$ + H, 37). Anal. Calcd for $C_{17}H_{45}N_5Si_3Zr$: C, 41.25; H, 9.16. Found: C, 40.77; H, 9.16.

(Dimethylamino)tris(trimethylsilyl)azahafnatrane, 21. The procedure was the same as that for **20** except that $Hf(NMe_2)_4$ was used instead of $Zr(NMe_2)_4$. Yield: 65%. Mp: 52−54 °C. ^{1}H NMR: δ 3.25 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $SiNCH_2$), 3.06 (s, 6 H, $N(CH_3)_2$), 2.27 (t, 6 H, $^{3}J_{HH}$ = 5.1 Hz, $N(CH_2)_3$), 0.23 (s, 27 H, $SiCH_3$). $^{13}C\{^{1}H\}$ NMR: δ 63.09 ($N(CH_2)_3$), 45.81 ($SiNCH_2$), 43.56 ($N(CH_3)_2$), 1.86 ($SiCH_3$). $^{29}Si\{^{1}H\}$ NMR: δ 1.92. MS (EI), *m/e* (ion, relative intensity): 582 (M^+, 3), 509 ($M^+ - SiMe_3$, 7), 494 ($M^+ - SiMe_3$ − Me, 19), 360 ($(N(CH_2CH_2NHSiMe_3)(CH_2CH_2NSiMe_3)_2^+$, 26). CIMS ($NH_3$, positive ion detection), *m/z* (ion, relative intensity): 583 (M^+ + H, 31), 538 ($M^+ - NMe_2$, 10). A single crystal suitable for X-ray diffraction was obtained by slow sublimation of **21**. Anal. Calcd for $C_{17}H_{45}HfN_5Si_3$: C, 35.06; H, 7.79. Found: C, 35.32; H, 7.85.

Attempted Preparation of (Dimethylamino)tris(*tert*-butyldimethylsilyl)azatitanatrane, 22. Method A. At −20 °C, 50 mL of toluene was added slowly to a mixture of **6** (1.34 g, 2.35 mmol) and $LiNMe_2$ (0.130 g, 2.55 mmol). The mixture was warmed to room temperature then refluxed for 5 days, and finally filtered through a pad of Celite. The volatile components in the filtrate were removed *in vacuo* to give a sticky red-orange oil (1.40 g). No target product could be identified from its ^{1}H and ^{13}C NMR spectra.

Method B. A solution of $Ti(NMe_2)_4$ (1.05 g, 4.70 mmol) in 20 mL of toluene was added to a stirred solution of (*t*-$BuMe_2Si)_3$-tren (2.26 g, 4.62 mmol) in 15 mL of toluene. The mixture was refluxed for 4

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Table 1. Crystal Data, Data Collection, Solution, and Structure Refinement Parameters for **21** and **25**

	21	**25**
empirical formula	$C_{17}H_{45}HfN_5Si_3$	$C_{18}H_{48}N_4OSi_4Ti$
fw	582.3	496.86
color; habit	colorless, prism	yellow, irregular
cryst size (mm)	0.28 × 0.12 × 0.09	0.20 × 0.11 × 0.05
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$Pna2_1$
α (Å)	11.837(2)	21.772(2)
b (Å)	14.284(3)	11.481(4)
c (Å)	15.750(4)	11.566(1)
vol (Å^3)	2662.9(9)	2891(1)
Z	4	4
d_{calcd} (g/cm^3)	1.453	1.142
abs coeff (mm^{-1})	8.612	4.210
F(000)	1184	1080
radiation	Cu Kα ($\lambda = 1.541\ 78$ Å)	Cu Kα ($\lambda = 1.541\ 78$ Å)
monochromator	graphite crystal	graphite crystal
2θ range (deg)	4.0 to 115.0	4.0 to 115.0
scan type	$2\theta-\theta$	$2\theta-\theta$
std reflcns	3 measd every 97 reflcns	3 measd every 97 reflcns
index ranges	$-12 \le h \le 12, -15 \le k \le 0, -17 \le l \le 0$	$-1 \le h \le 23, -1 \le k \le 12, -1 \le l \le 12$
no. of reflcns collctd	3905	2702
no. of indep reflcns	3569	2286
R_{int}	0.0375	0.0330
no. of obsd reflcns	3448 ($F \ge 4.0\sigma(F)$)	2019 ($I \ge 2\sigma(I)$)
min/max transm	0.4726/0.9524	0.914/0.539
syst used	Siemens SHELXTL-Plus (VMS)[15]	SHELXL-93[16]
refinement method	full-matrix least-squares	full-matrix least-squares
weighting scheme, w^{-1}	$[\sigma^2(F) + 0.0003F^2]$	$[\sigma^2(F_o^2) + (0.0558p)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
params refined	293	291
final R indices (obsd data)	$R^a = 0.0352, R_w{}^b = 0.0421$	$R1^c = 0.0341$ $WR2^d = 0.0835$
	$R^a = 0.0363, R_w{}^b = 0.0424$	$R1^c = 0.0400$ $WR2^d = 0.0857$
goodness-of-fit	1.57^e	1.055^f
largest and mean Δ/σ	0.014, 0.001	0.001, 0.000
largest difference peak (e/Å^{-3})	1.12	0.324
largest difference hole (e/Å^{-3})	−1.45	−0.272

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \Sigma[w^{1/2}(|F_o| - |F_c|)]/\Sigma(w^{1/2}|F_o|)$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $WR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [e] Goodness-of-fit $= [\Sigma(w|F_o - F_c|^2)/(n - p)]^{1/2}$. [f] Goodness-of-fit $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

days. The solvent was removed *in vacuo* to give a sticky oil. The ^{1}H NMR spectrum of the product revealed only the presence of starting materials.

(Dimethylamino)tris(*tert*-butyldimethylsilyl)azazirconatrane, 23. The procedure was the same as that for **17** except that (t-BuMe$_2$Si)$_3$-tren was used instead of i-Pr$_3$-tren. Yield: 91%. Mp: > 82 °C dec. ^{1}H NMR: δ 3.31 (t, 6 H, $^3J_{HH} = 5.1$ Hz, SiNCH_2), 3.00 (s, 6 H, N(CH_3)$_2$), 2.33 (t, 6 H, $^3J_{HH} = 5.1$ Hz, N(CH_2)$_3$), 1.04 (s, 27 H, C(CH_3)$_3$), 0.23 (s, 18 H, SiCH_3). ^{13}C{^{1}H} NMR: δ 62.72 (N(CH$_2$)$_3$), 47.51 (SiNCH$_2$), 44.73 (N(CH$_3$)$_2$), 28.15 (C(CH$_3$)$_3$), −2.70 (SiCH$_3$), −3.04 (CH). ^{29}Si{H} NMR: δ 4.74. MS (EI), m/z (ion, relative intensity) 621 (M$^+$, 2), 606 (M$^+$ − Me, 2), 577 (M$^+$ − NMe$_2$, 83), 576 (M$^+$ − 3Me or M$^+$ − HNMe$_2$, 100), 516 (M$^+$ − SiMe − t-Bu + H, 42). Anal. Calcd for $C_{26}H_{63}N_5Si_3Zr$: C, 50.26; H, 10.22. Found: C, 50.31; H, 10.27.

(Dimethylamino)tris(*tert*-butyldimethylsilyl)azahafnatrane, 24. The procedure was the same as that for **23** except that Hf(NMe$_2$)$_4$ was used instead of Zr(NMe$_2$)$_4$. Yield: 82%. Mp: > 75 °C dec. ^{1}H NMR: δ 3.31 (t, 6 H, $^3J_{HH} = 5.1$ Hz, SiNCH_2), 2.99 (s, 6 H, N(CH_3)$_2$), 2.34 (t, 6 H, $^3J_{HH} = 5.1$ Hz, N(CH_2)$_3$), 1.04 (s, 27 H, C(CH_3)$_2$), 0.22 (s, 18 H, SiCH_3). ^{13}C{^{1}H} NMR: δ 62.74 (N(CH$_2$)$_3$), 47.52 (SiNCH$_2$), 44.75 (N(CH$_3$)$_2$), 28.17 (C(CH$_3$)$_3$), −2.68 (SiCH$_3$), −3.11 (C(CH$_3$)$_3$). ^{29}Si{^{1}H} NMR: δ 4.79. MS (EI), m/z (ion, relative intensity): 564 (M$^+$ − SiMe$_2$(t-Bu) − 2Me, 1), 485 (M$^+$ − NMe$_2$ − Hf, 2), 224 (HfNMe$_2^+$, 2).

(Trimethylsiloxy)tris(trimethylsilyl)azatitanatrane, 25. The accidentally discovered procedure for obtaining this compound was given in method A for **19**. A rational synthesis of **25** consists of adding THF (40 mL) to a Schlenk flask containing 0.36 g (0.81 mmol) of **3** and 0.12 g (97%, 1.0 mmol) of NaOSiMe$_3$. After the reaction mixture was refluxed for 19 h, the solvent was removed *in vacuo*. The residue was dispersed in 8 mL of pentane, and the suspension was filtered through a pad of Celite. The residue was copiously washed with pentane and the volatile components in the filtrate were removed *in vacuo* to give 0.40 g of the yellow product **25** in quantitative yield. Crystals of **25** were obtained by recrystallization of the product in pentane. Mp: 161−163 °C. ^{1}H NMR: δ 3.27 (t, 6 H, $^3J_{HH} = 5.1$ Hz, SiNCH_2), 2.41 (t, 6 H, $^3J_{HH} = 5.1$ Hz, N(CH_2)$_3$), 0.52 (s, 9 H, OSi(CH_3)$_3$), 0.26 (s, 27 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR: δ 62.43 (N(CH$_2$)$_3$), 50.06 (SiNCH$_2$), 4.42 (OSi(CH$_3$)$_3$), 1.66 (Si(CH$_3$)$_3$). HRMS (EI), m/z: calcd for $C_{18}H_{48}N_4OSi_4Ti$, 496.23848; found; 496.23986; error, 2.7 ppm. MS (EI), m/z (ion, relative intensity): 496 (M$^+$, 42), 407 (M$^+$ − OSiMe$_3$, 38). CIMS (NH$_3$, positive ion detection), m/z (ion, relative intensity): 497 (M$^+$ + H, 100), 407 (M$^+$ − OSiMe$_3$, 34).

Single-Crystal X-ray Diffraction Studies of 21 and 25. A crystal of **21** and **25** was attached to the tips of separate glass fibers. The fibers were mounted on a Siemens P4RA diffractometer for data collection at −60 ± 1 °C. The cell constants for the data collections were determined from reflections found from rotation photographs. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0−50.0° in 2θ. Lorentz and polarization corrections were applied to the data as were nonlinear corrections based on the decay in the standard reflections. A series of azimuthal reflections was collected, and a semiempirical absorption correction based on the azimuthal scans was applied to the data.

The space groups $P2_12_12_1$ and $Pna2_1$ were chosen for **21** and **25**, respectively, based on systematic absences and intensity statistics. These assumptions proved to be correct as shown by a successful direct-methods solution[15] and subsequent refinement. All non-hydrogen atoms were placed directly from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were treated as riding-atoms with C−H distances equal to 0.96 Å and

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(15) *SHELXTL PLUS*; Siemens Analytical X-ray, Inc.: Madison, WI, USA.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **21**

	Bond Lengths		
Hf−N(1)	2.488(6)	Hf−N(2)	2.084(7)
Hf−N(3)	2.085(7)	Hf−N(4)	2.060(7)
Hf−N(5)	2.048(6)	N(4)−Si(4)	1.729(7)
N(2)−Si(2)	1.730(8)	Si(3)−N(3)	1.732(6)
	Bond Angles		
N(1)−Hf−N(2)	73.2(2)	N(1)−Hf−N(3)	76.3(2)
N(2)−Hf−N(3)	115.5(3)	N(1)−Hf−N(4)	74.9(2)
N(2)−Hf−N(4)	115.2(3)	N(3)−Hf−N(4)	109.4(3)
N(1)−Hf−N(5)	173.0(3)	N(2)−Hf−N(5)	100.0(3)
N(3)−Hf−N(5)	108.5(2)	N(4)−Hf−N(5)	107.4(3)
Hf−N(2)−C(2)	114.6(6)	Hf−N(2)−Si(2)	128.5(4)
C(2)−N(2)−Si(2)	116.2(6)	Hf−N(3)−C(4)	112.1(5)
Hf−N(3)−Si(3)	129.8(3)	C(4)−N(3)−Si(3)	118.1(5)
Hf−N(4)−C(6)	113.4(5)	Hf−N(4)−Si(4)	128.3(4)
C(6)−N(4)−Si(4)	116.1(6)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **25**

	Bond Lengths		
Ti−O	1.833(5)	N(2)−Si(1)	1.730(4)
Ti−N(3)	1.928(4)	N(3)−Si(2)	1.731(4)
Ti−N(2)	1.944(4)	N(4)−Si(3)	1.724(4)
Ti−N(4)	1.946(4)	O−Si(4)	1.635(4)
Ti−N(1)	2.451(5)		
	Bond Angles		
O−Ti−N(3)	105.0(2)	C(2)−N(2)−Si(1)	118.5(3)
O−Ti−N(2)	104.3(2)	C(2)−N(2)−Ti	114.4(3)
N(3)−Ti−N(2)	112.8(2)	Si(1)−N(2)−Ti	127.1(3)
O−Ti−N(4)	103.3(2)	C(4)−N(3)−Si(2)	115.8(3)
N(3)−Ti−N(4)	114.3(2)	C(4)−N(3)−Ti	114.0(3)
N(2)−Ti−N(4)	115.4(2)	Si(2)−N(3)−Ti	129.4(2)
O−Ti−N(1)	178.6(2)	C(6)−N(4)−Si(3)	116.7(3)
N(3)−Ti−N(1)	76.0(2)	C(6)−N(4)−Ti	114.5(3)
N(2)−Ti−N(1)	76.1(2)	Si(3)−N(4)−Ti	128.0(2)
N(4)−Ti−N(1)	75.3(2)	Si(4)−O−Ti	176.0(2)

individual isotropic thermal parameters. In the case of the hydrogen atoms of methyl substituents, the groups were refined torsionally prior to converting to a riding-atom model. Final refinements were done with SHELXL-93.[16] After refinement was nearly complete for **25**, it was determined that the sample was a racemic mixture to the extent of 6(2)% and refined as such. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL-Plus[15] and SHELXL-93[16,17] programs. Crystal data and experimental conditions for data collection, solution, and structure refinement are listed in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3 for **21** and **25**, respectively. Positional parameters are collected in Tables 4 and 5 for **21** and **25**, respectively.

Results and Discussion

Syntheses. Compound **16**−**21**, **23** and **24** were synthesized by transaminations of $M(NMe_2)_4$ with the corresponding tripodal tetramines according to reaction 1 in yields from 35% to 91%.

$$\text{M(NMe}_2)_4 + (\text{RHNCH}_2\text{CH}_2)_3\text{N} \xrightarrow[\text{reflux}]{\text{THF or toluene}} \overline{\text{Me}_2\text{NM(RNCH}_2\text{CH}_2)_3\text{N}} + 3\text{Me}_2\text{NH} \quad (1)$$

$$\text{M} = \text{Ti, Zr, Hf; R} = i\text{-Pr, SiMe}_3\text{, SiMe}_2(t\text{-Bu})$$

All of the compounds exhibited monomeric characteristics, as determined by their NMR spectra and the crystal structure of **21** in the solid state. This is consistent with the observation that for most of the compounds, further purification can be accomplished by sublimation, indicating their volatile nature.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **21**

atom	x	y	z	U_{eq}[a]
Hf	201(1)	157(1)	9112(1)	22(1)
N(1)	496(6)	867(5)	7687(4)	29(2)
C(1)	1656(8)	646(7)	7410(6)	39(3)
C(2)	2387(8)	549(8)	8186(6)	43(4)
N(2)	1855(6)	−154(6)	8754(4)	33(2)
Si(2)	2606(2)	−1177(2)	8917(2)	31(1)
C(21)	3298(12)	−1574(9)	7923(7)	67(5)
C(22)	3729(10)	−1045(8)	9738(7)	54(4)
C(23)	1624(8)	−2146(6)	9238(7)	45(4)
C(3)	329(9)	1887(6)	7810(5)	36(3)
C(4)	−523(8)	2042(6)	8514(5)	36(3)
Si(3)	−38(2)	2240(2)	10219(1)	29(1)
C(31)	−475(9)	3479(6)	10045(7)	46(4)
C(32)	1451(8)	2283(7)	10592(7)	45(4)
C(33)	−919(9)	1762(8)	11093(6)	47(4)
N(3)	−144(6)	1572(5)	9304(4)	30(2)
C(5)	−382(8)	463(6)	7124(5)	39(3)
C(6)	−693(9)	−515(7)	7455(5)	39(3)
N(4)	−1036(6)	−419(5)	8355(4)	29(2)
Si(4)	−2465(2)	−516(2)	8561(2)	33(1)
C(41)	−3342(8)	170(8)	7790(7)	52(4)
C(42)	−2773(8)	−33(8)	9636(6)	46(4)
C(43)	−2935(9)	−1756(7)	8484(7)	45(4)
N(5)	139(6)	−513(5)	10261(4)	29(2)
C(51)	−572(9)	−1289(7)	10542(6)	40(3)
C(52)	986(8)	−336(7)	10915(6)	45(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Compound **19** obtained from reaction 1 contained a considerable amount of impurities, as judged by ^{1}H NMR spectroscopy, and further purification by distillation was not successful. Compound **19** was also obtained in impure form by a metathesis reaction as shown in reaction 2. Although compound **19** solidified upon standing, a small number of crystals of **25** which crystallized first could be isolated from **19**. The same result was obtained despite repeated attempts to exclude moisture. It seems likely that adventitious water present during work up led to the formation of **25**, owing to the extreme moisture- and air-sensitivity of **19**. The structure of **25** was confirmed by single-crystal X-ray diffraction experiments. The process for the formation of **25** is not yet clear. However, at least two kinds of reactions can be proposed. The first reaction route involves the hydrolysis of one of the trimethylsilyl groups in **19** to form the intermediate trimethylsilanol, which subsequently reacts with **19** to form **25** with the evolution of $HNMe_2$, as shown in Scheme 1. The product **26** formed in the hydrolysis could be expected to be unstable because of the presence of an active proton on the amido nitrogen and the NMe_2 group on Ti atom which can combine to eliminate $HNMe_2$ through an intermolecular or intramolecular process to form dimeric **28**. An analogous dimerization has been observed in the transamination of $Ti(NMe_2)_4$ with i-Pr_2-tren.[18] However, no spectral parameters consistent with **28** were detected by ^{1}H or $^{13}C\{^1H\}$ NMR. Possibly, oligomerization reactions are responsible for the trace amounts of uncharacterized impurities in compound **19**, as observed by ^{1}H and $^{13}C\{^1H\}$ NMR spectra. A second type of possible pathway to **25** includes an amination and a hydrolysis, followed by hydrolysis of one of the trimethylsilyl groups on **19** to form **25** and **26** (Scheme 2). The latter could oligomerize

$$\underset{\mathbf{3}}{\overline{\text{ClTi(Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}}} + \text{LiNMe}_2 \xrightarrow[\text{reflux}]{\text{toluene}} \mathbf{19} + \text{LiCl} \quad (2)$$

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(16) SHELXL-93. Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

(17) All X-ray scattering factors and anomalous dispersion terms were obtained from: *International Table for Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. C, pp 4.2.6.8 and 6.1.1.4.

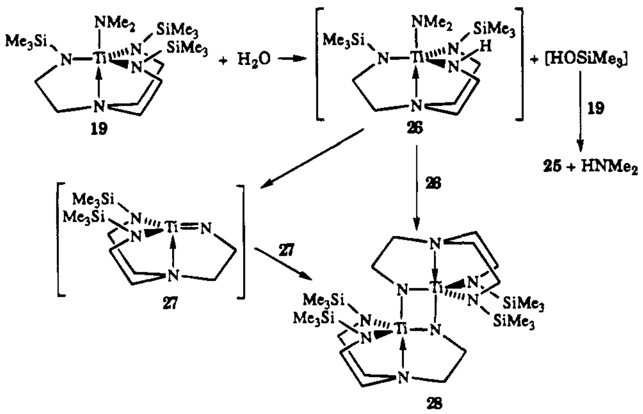
(18) Duan, Z.; Verkade, J. G. *Inorg. Chem.*, in press.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **25**

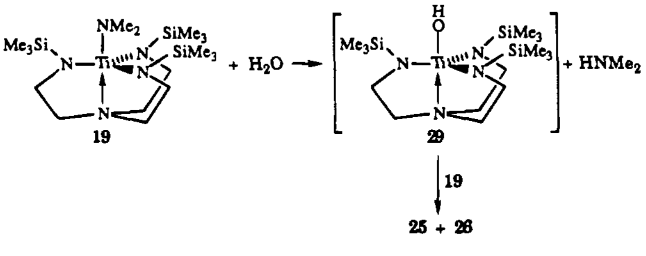
atom	*x*	*y*	*z*	*U*(eq)[a]
Ti	8495(1)	7591(1)	551(1)	22(1)
N(1)	8627(2)	7800(4)	2645(4)	28(1)
C(1)	8001(2)	7671(5)	3149(5)	41(2)
C(2)	7637(2)	6906(5)	2332(5)	38(2)
N(2)	7668(2)	7425(3)	1161(4)	26(1)
Si(1)	6989(1)	7826(1)	493(2)	30(1)
C(11)	6401(3)	8287(7)	1578(7)	66(2)
C(12)	6654(3)	6604(5)	−343(6)	55(2)
C(13)	7126(3)	9115(5)	−461(6)	51(2)
C(3)	9044(3)	6853(5)	2995(5)	37(1)
C(4)	9439(2)	6566(5)	1948(5)	36(1)
N(3)	9024(2)	6312(4)	968(4)	28(1)
Si(2)	9002(1)	4875(1)	517(2)	34(1)
C(21)	9030(3)	3840(5)	1772(7)	59(2)
C(22)	9671(3)	4547(6)	−450(7)	65(2)
C(23)	8267(3)	4590(5)	−249(6)	54(2)
C(5)	8891(2)	8960(5)	2836(5)	37(1)
C(6)	8693(2)	9718(5)	1832(5)	37(1)
N(4)	8864(2)	9122(3)	749(4)	28(1)
Si(3)	9493(1)	9753(1)	−63(2)	35(1)
C(31)	10051(3)	10378(7)	876(6)	69(2)
C(32)	9816(2)	8640(5)	−981(6)	43(1)
C(33)	9135(3)	10984(5)	−947(7)	64(2)
O	8399(2)	7472(3)	−1019(4)	33(1)
Si(4)	8356(1)	7420(2)	−2429(2)	40(1)
C(51)	8345(3)	8897(6)	−3064(6)	56(2)
C(52)	7646(3)	6687(7)	−2914(6)	68(2)
C(53)	9016(3)	6589(6)	−3040(6)	59(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Scheme 1



Scheme 2



as discussed previously. A rational synthesis of **25** in quantitative yield was carried out by the metathesis shown in reaction 3.

$$\overline{\mathrm{ClTi(Me_3SiNCH_2CH_2)_3N}} + \mathrm{NaOSiMe_3} \xrightarrow[\text{reflux}]{\text{THF}} \mathbf{25} + \mathrm{NaCl} \quad (3)$$

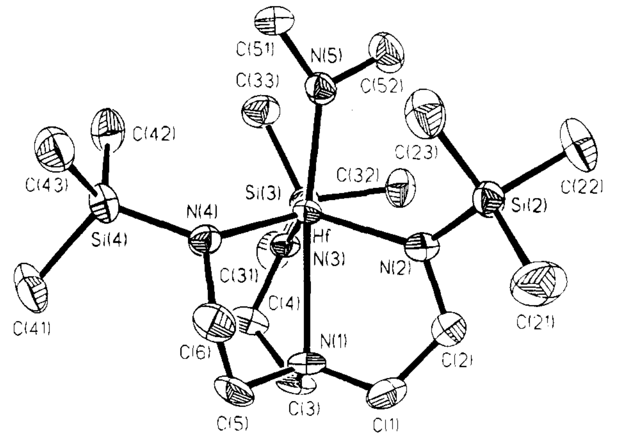


Figure 1. Molecular structure of $\mathrm{Me_2N\overline{Hf(Me_3SiNCH_2CH_2)_3N}}$, **21**. Ellipsoids are drawn at the 50% probability level.

It is interesting to note that for titanium complexes obtained by transaminations, the formation rates decrease in the order **1** > **16** > **19** > **22** (or R = Me > *i*-Pr > $\mathrm{SiMe_3}$ > $\mathrm{SiMe_2(\mathit{t}\text{-}Bu)}$). Thus, the reaction was completed in about 3 h in refluxing THF for compound **1**,[3] only 50% of the starting materials was consumed in refluxing toluene over 3 days for **16**, and no product was observed in 4 days in THF for **19**. When the solvent was changed from THF to toluene in order to raise the reaction temperature, a small amount of **19** was obtained over 4 days according to ^{1}H NMR spectroscopy. In the presence of $(t\text{-}\mathrm{BuMe_2Si})_3$-tren, $\mathrm{Ti(NMe_2)_4}$ gave no evidence for the expected reaction product, **22**, even after 4 days in refluxing toluene. This suggests that nucleophilic attack of a lone electron pair from one of the tripod amine HNR groups on the titanium atom is probably a more important step in the transamination reaction than a proton transfer from one of the HNR groups of the tetraamine to a nitrogen atom of an $\mathrm{NMe_2}$ group of $\mathrm{Ti(NMe_2)_4}$. This is in contrast to recent observations on analogous aluminum systems[14] in which the proton transfer pathway dominates nucleophilic attack by the amine. This contrasting behavior is attributable to the greater Lewis acidity of the aluminum substrate. According to the above argument, the formation rates of azatitanatranes are expected to increase with increasing basicity of the corresponding tetramines, i.e., **16** > **1** > **22** > **19**. Thus in silylated tetramines, the basicity of the HNR nitrogens is diminished by π-bonding to the silicon atom, while alkylated tetramines are expected to be electron rich. Steric effects apparently play a dominant role in the order of the rates of formation observed (**1** > **16** > **19** > **22**). The Zr and Hf complexes possess higher observed formation rates than the corresponding Ti analogs, probably owing to their larger metal sizes.

Structural Considerations. The molecular structure of **21** shown in Figure 1, the first for a hafnium tetramide, exhibits a central hafnium atom in a slightly distorted TBP geometry. Like **1**,[18] this molecule possesses virtual C_s symmetry with the mirror plane passing through the N(1)−Hf−N(5) atoms and the C(3)−C(4)−N(3) arm. The axial N(1)−Hf−N(5) bond angle is not quite linear in **21** (173.0(3)°) as is the case for **1** (174.0(1)°), and the protrusion of the Hf atom above the equatorial nitrogen plane (0.545 Å) is larger than that of Ti in **1** (0.436 Å). This leads to an average $\mathrm{N_{eq}{-}Hf{-}N(5)}$ angle of 105.(3)° in **21**. It is interesting to note that the geometries around the equatorial nitrogens (average of sum of angles = 359.0(5)°) and the $\mathrm{Me_2N}$ nitrogen (sum of angles = (359.5(6)°) are the same, suggesting nearly equal π-bonding opportunities for the two types of nitrogen with hafnium as was also the case with titanium in **1**. The average $\mathrm{Hf{-}N_{eq}}$ bond distance (2.076(7) Å) is comparable to the $\mathrm{Me_2N{-}Hf}$ bond length (2.048(6) Å) but it is considerably shorter than the transannular $\mathrm{Hf{-}N_{ax}}$ bond (2.488(6) Å).

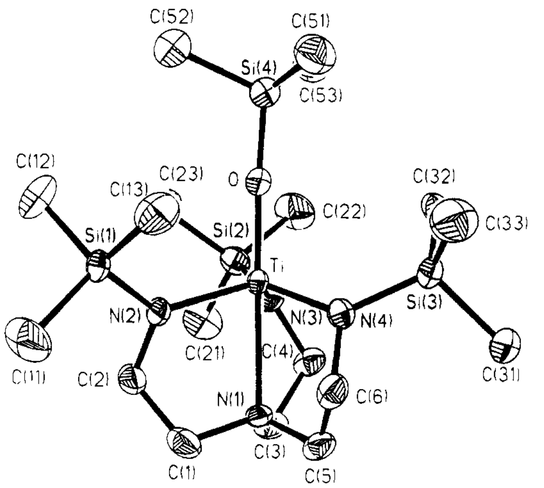
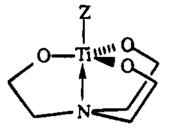
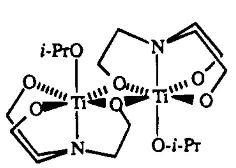


Figure 2. Molecular structure of $Me_3SiO\overline{Ti(Me_3SiNCH_2CH_2)_3N}$, **25**. Ellipsoids are drawn at the 50% probability level.

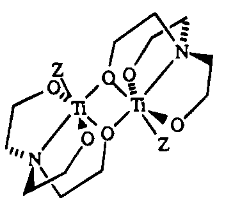
Like **21**, **25** (Figure 2) features a distorted TBP geometry but in contrast, **25** has virtually ideal C_{3v} symmetry with the O−Ti−N(1) angle only 1.4° short of linearity and the O−Ti−Si angle 4° from linearity. The Ti atom is displaced upwards from the equatorial nitrogen plane (sum of angles = 332.5(2)°) by 0.476 Å toward the $OSiMe_3$ group. As is typical in azametallatrane complexes, the equatorial nitrogens are quite planar in **25** with the average sum of the angles around them equal to 359.5(3)°. The average $Ti-N_{eq}$ bond length of 1.939(4) Å is within experimental error of the analogous average distance reported for **1** (1.949(2) Å[18]), **8** (1.923(8) Å[4c]), **10** (1.920(6) Å[4c]), and **11** (1.901(9)[4c]),[19] while the transannular $Ti-N_{ax}$ bond distance of 2.451(5) Å in **25** is longer than that in **1** (2.257(2) Å[18]), **8** (2.227(11) Å[4c]), **10** (2.229(6) Å[4c]), **11** (average 2.209(9) Å[4c]),[19] **29** (2.264(3) Å[20]), and **30** (2.2821(3) Å[21]). Surprisingly, the transannular $Ti-N_{ax}$ bond in **25** is also longer than those in the titanatrane dimers **31** (2.333(1) Å[22]) and **32** (2.270(2) Å[3]) which is somewhat surprising since this bond in the latter compounds could be expected to be longer owing to their higher coordination number of six. In contrast, the $Ti-O_{ax}$ bond length of 1.833(5) Å in **25** is comparable to the $Ti-O_{ax}$ bonds in **29** (1.834(2) Å[20]) and **31** (1.833(1) Å[22]), shorter than those in **11** (1.987(7) Å[4c]) and **32** (1.939(1) Å[21]), and somewhat shorter than the average Ti−O distance (1.877(9) Å) reported for a five-coordinate titanium(IV) alkoxide compound[23] but longer than that in **30** (1.776(2) Å[21]). The $Ti-O_{ax}$ bond in **25** is comparable with the average $Ti-O_{eq}$ bonds in **29** (1.834(1) Å[20]) and **30** (1.836(3) Å[21]) but it is shorter than the average $Ti-O_{eq}$ bonds in **31** (1.959(1) Å[22]) and **32** (1.970(1) Å[3]).



	Z
29[20]	$OSiPh_3$
30[21]	1/2 $OCMe_2CMe_2O$



31[22]



32[21] (Z = NMe_2)

Mass Spectra. The EI mass spectra of each of the compounds except **19** exhibited a molecular peak for the corresponding complex in accord with the volatility of these compounds. In general it is difficult to distinguish an oxygen atom from a nitrogen atom using X-ray diffraction techniques. In this regard it was possible to consider an $HNSiMe_3$ or an $OSiMe_3$ axial substituent on the Ti atom in **25**. However, the EI mass spectrum of **25** showed a moderately intense parent peak at *m/z* 496 and the molecular $M^+ + H$ peak is the base peak in its $CI-NH_3$ spectrum. These results along with its high resolution mass spectrum confirmed the presence of the $OSiMe_3$ substituent in this compound.

NMR Spectra. In the ^1H NMR spectra of compounds **16**–**21**, **23**, and **24**, the AA′XX′ spin system for the methylene protons of the azametallatrane cage manifests itself as two virtual triplets, indicating virtual C_{3v} symmetry in solution at ambient temperature. This pattern is a general feature of monomeric atrane and azatrane complexes,[3,4,14,20,21,24] and it is consistent with the structure of **21** in the solid state if rotation of the Me_2N group is fast on the NMR time scale. The observed separations of 5.1 Hz within these triplets in the silyl-substituted compounds is independent of both the metal center and the substituent groups on equatorial nitrogens. It is interesting to note that except for the methyl protons on the equatorial nitrogen substituents, the ^1H chemical shifts for complexes of the same tetraamine ligand are generally in the order Ti > Zr ≈ Hf. This is consistent with a parallel order of the metal electronegativities[25] and an accompanying decreasing electron-withdrawing effect. This ordering of ^1H chemical shifts is reflected even more strongly in the ^{13}C chemical shifts, including those of compounds bearing methyl carbons on the equatorial nitrogens. The ^{29}Si chemical shifts (see Experimental Section) for the silylated species follow the same trend. Both ^1H and $^{13}C\{^1H\}$ spectra of **25** revealed C_{3v} symmetry in solution, consistent with its structure in the solid state.

Conclusions

It has been shown that a variety of volatile azatranes of group 4 can be synthesized by metathesis reactions. For titanium complexes, the formation rates depend upon the substituent groups on equatorial nitrogens and follow the order of Me > *i*-Pr > $SiMe_3$ > $SiMe_2(t\text{-}Bu)$. The mass and the NMR spectral data are consistent with monomeric behavior for these complexes.

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Supporting Information Available: Text giving experimental details for the structure solution, figures showing unit cells, and tables of structure determination data, bond distances, bond angles, hydrogen atom positional parameters, and general displacement parameter expressions (28 pages). Ordering information is given on any current masthead page.

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(19) The value reported in ref 4c is incorrect owing to a labeling error.

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