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Synthesis and Characterization of a Novel Azatitanatrane

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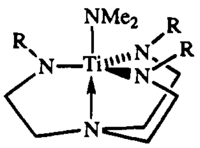
Azatitanatrane $[Ti(i\text{-}PrNCH_2CH_2)_2NCH_2CH_2N]_2$ (**13**) is obtained in 44% yield by the reaction of $Ti(NMe_2)_4$ with the new ligand $(i\text{-}PrNHCH_2CH_2)_2NCH_2CH_2NH_2$. Compound **13**, which features a dimeric structure as determined by ^1H, $^{13}C\{^1H\}$, and $^1H^1H$ NOESY NMR techniques and mass spectroscopy, exhibits a rigid configuration in solution on the NMR time scale. The structure of the azatitanatrane $Me_2NTi(MeNCH_2CH_2)_3N$ (**1**) was determined by single-crystal X-ray crystallography and was shown to exhibit unusually short axial Ti−N bonds. Crystal data: monoclinic, space group $P2_1/c$, $a = 7.9550(7)$ Å, $b = 10.546(2)$ Å, $c = 18.105(2)$ Å, $\beta = 97.365(8)°$, $V = 1506.4(3)$ Å^3, $Z = 4$, $R = 0.0373$.

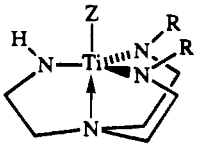
Introduction

Titanium nitride, TiN, exhibits interesting properties such as metallic behavior, a high melting point, hardness, and inertness to most chemicals, allowing many potential applications. For example, it can be used as a wear-resistant coating on tools,[1] as a gold substitute for decorative coatings and for thin film resistors,[2,3] as reflectance and hardness coatings for microelectronic devices,[4,5] and as a diffusion barrier in various semiconductor metalization schemes.[6−9] During our exploration of the chemistry of atranes,[10] we became interested in synthesizing candidates for the MOCVD of metallic and non-metallic nitrides. In the case of titanium, such compounds are represented by structures **1**-**4**.



	R
1	Me
2	$CHMe_2$
3	$SiMe_3$
4	$SiMe_2(t\text{-}Bu)$

Compounds **1**−**3** have been synthesized and characterized by us,[11] but compound **4** has thus far resisted synthesis, probably owing to the more bulky nature of the tetraamine ligand in **4** than in **1**−**3**. Compound **1** was evaluated as a potential precursor for the growth of TiN thin film. However, the TiN film obtained from liquid **1** was contaminated with titanium carbide perhaps from impurities in **1**.[11c] Thus compound **1** of better purity may be required. We demonstrate here that **1** is actually crystalline at room temperature and also report its crystal structure. Experiments on the growth of TiN thin films from **1** revealed that when ammonia was passed through the reactor during MOCVD, the N/Ti ratio of the film improved.[11c] This prompted us to consider new precursors such as **5**-**8** which might generate ammonia during pyrolysis by elimination of an NH_2 group from the axial position and a hydrogen from an equatorial nitrogen.



	R	Z
5	H	NH_2
6	$CHMe_2$	NH_2
7	CH_3	NH_2
8	$SiMe_3$	NH_2

	R	Z
9	H	Cl
10	$CHMe_2$	Cl
11	$CHMe_2$	NMe_2

Because of the very unstable and explosive properties of $Ti(NH_2)_4$,[12] we did not attempt a transamination approach to the synthesis of **5**-**8**. Instead, complexes **9** and **10** were considered to be the best starting materials for our initial attempts, owing to the possibility of nucleophilically substituting the chloride with an amide. Here we show, however, that **9** was obtained as an oligomer or polymer and that attempts to make **10** failed because of polymerization as well as some unexpected reactions. Thus we turned our attention to the synthesis of **11** by transamminating $Ti(NMe_2)_4$ with the new tren derivative $(i\text{-}PrNHCH_2CH_2)_2NCH_2CH_2NH_2$ (i-Pr_2-tren, **12**). The model compound **11** might be expected to eliminate gaseous $HNMe_2$ under pyrolysis conditions and because of this might give improved MOCVD properties to the extent that Me_2NH could mimic NH_3 in providing a source of nitrogen. However, we show here that **11** is unstable with respect to the elimination product **13** which is formed immediately as determined by NMR and mass spectroscopies. Although azametallatrane dimers derived from trisubstituted tren ligands have recently been reported from this group for group 13 elements,[13] compound **13** is the first example of a dimeric complex obtained directly

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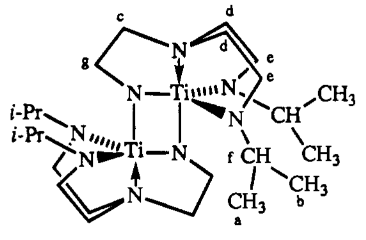

13

from a disubstituted tren ligand. We also show that **13** is rigid in solution on the NMR time scale.

Experimental Section

General Procedures. All reactions were carried out under argon with strict exclusion of moisture using standard Schlenk or drybox techniques.[14] Solvents were dried over and distilled from Na/benzophenone under nitrogen and stored over 4 Å molecular sieves under an argon atmosphere prior to use. *n*-Butyllithium as 2.5 or 2.0 M solutions in hexane or cyclohexane, respectively, were purchased from Aldrich. Tren ($(H_2NCH_2CH_2)_3N$) was distilled under vacuum after receipt as a kind gift from the Hampshire Chemical Co. $Ti(NMe_2)_4$[15] and Me_3-tren ($(MeNHCH_2CH_2)_3N$)[16] were prepared using literature methods.

NMR spectra were recorded at 20 °C (unless otherwise stated) on a Nicolet NT 300 (^1H) or a Varian VXR 300 with deuterated solvents as an internal lock. The 2D NOESY experiment was performed with a mixing time of 0.5 s. ^1H NMR (299.949 MHz) spectra were referenced to the chemical shift of the residual proton signal from the deuterated solvent or from Me_4Si as the internal reference. ^{13}C (75.429 MHz) spectra were referenced to solvent signals. Mass spectra were obtained on a Finnigan 4000 instrument or a Kratos MS-50 spectrometer. FT-IR spectra were taken on an IBM IR-98 or a DigiLab FTS-7 FTIR spectrometer using KBr pellets. Melting points were measured in sealed capillaries with a Thomas-Hoover apparatus.

Purification of 1. This compound, synthesized according to our published method,[11a] in our hands was isolated as an oily slurry which was then placed on filter paper to absorb the oil. Sublimation of the remaining crude solid at 80 °C/10 × 10^{-3} mmHg followed by recrystallization of the sublimate from pentane at −30 °C gave an overall yield (based on Me_3-tren) of 52%: ^1H NMR (C_6D_6) δ 3.284 (s, 9 H, CH_3), 3.278 (s, 6 H, $N(CH_3)_2$), 3.160 (t, 6 H, $^3J_{HH}$ = 6.0 Hz, $MeNCH_2$), 2.595 (t, 6 H, $^3J_{HH}$ = 6.0 Hz, $N(CH_2)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 58.71 ($N(CH_2)_3$), 52.46 ($MeNCH_2$), 45.40 (NCH_3), 43.58 ($N(CH_3)_2$).

Attempted Preparation of 9. A solution of tren (1.499 g, 10.25 mmol) and triethylamine (3.536 g, 34.94 mmol) in 10 mL of THF was added to a suspension of $TiCl_4(THF)_2$ (3.336 g, 9.990 mmol) in 40 mL of THF. A red-orange precipitate formed immediately which was dispersed by placing the reaction vessel in an ultrasound cleaning bath. The reaction mixture was then stirred at room temperature for 1 day, filtered, and washed with THF (3 × 10 mL) to give 4.90 g of orange solid, in which Et_3NHCl was observed by ^1H NMR (DMSO-d_6) spectroscopy. The crude product was stirred with 100 mL of CH_3CN at 65 °C, filtered warm, washed with warm CH_3CN, and dried *in vacuo* to give the orange product in quantitative yield. ^1H NMR (DMSO-d_6) δ 8.29 (s, br, 3 H, NH), 3.01 (s, br, 6 H, $HNCH_2$), 2.67 (s, br, 6 H, $N(CH_2)_3$); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 51.32 ($N(CH_2)_3$), 36.67 ($HNCH_2$).

Attempted Preparation of 10. A 2.5 M solution of *n*-BuLi in hexane (8.05 mL, 20.1 mmol) was added slowly to a stirred solution of **12** (1.55 g, 6.71 mmol) in 50 mL of toluene which had been precooled to −50 °C. The reaction mixture was allowed to warm to room temperature where stirring was continued for 3.5 h. The solution was then cooled to −70 °C, and $Ti(NMe_2)_4$ (2.38 g, 7.12 mmol) was added. The color of the solution changed from yellow to brown. After the reaction mixture was stirred at −70 °C for 8 h, it was warmed to room temperature over a period of 3 h and stirred for an additional 85 h. The reaction mixture was then filtered, and the volatile components from the filtrate were removed *in vacuo* to give 2.0 g of a dark-red solid. Both the ^1H and ^{13}C NMR spectra of the product in C_6D_6 showed very complicated resonance patterns.

***i*-Pr₂-tren (12).** To an ice-cooled stirred solution of tren (32.5 g, 0.222 mol) in an acetate buffer (sodium acetate, 81.0 g; acetic acid 225 mL; H_2O, 600 mL) was added 350 mL of acetone (4.73 mol). $NaBH_4$ (110 g, 2.91 mol) was added in small portions over a period of 9 h, and then a 20% (by weight) aqueous solution of NaOH (500 mL) was added resulting in the separation of an oily layer. This mixture was extracted by five 200 mL portions of Et_2O. The extract was dried with Na_2SO_4 and the Et_2O was removed under vacuum leaving a crude product which was distilled at 79−105 °C at 50 mTorr, giving a mixture of *i*-Pr_3-tren and *i*-Pr_2-tren, in the approximate ratio 3:2 based on ^1H NMR data taken in C_6D_6. The mixture was then dissolved in 700 mL of hexane, and the resulting solution was stirred vigorously for 65 h with NaI (22.1 g). A white precipitate was filtered off, and *i*-Pr_3-tren was recovered from the filtrate upon evaporation of the solvent *in vacuo*. The white precipitate was a NaI adduct of *i*-Pr_2-tren as determined by its ^1H and $^{13}C\{^1H\}$ NMR spectra in D_2O: ^1H NMR (D_2O) δ 2.93 (septet, 1 H, $^3J_{HH}$ = 6.3 Hz, CH), 2.73 (t, 4 H, $^3J_{HH}$ = 6.5 Hz, *i*-$PrNCH_2$), 2.68 (t, 2 H, $^3J_{HH}$ = 6.9 Hz, H_2NCH_2), 2.60 (t, 4 H, $^3J_{HH}$ = 6.5 Hz, $N(CH_2CH_2NH$-*i*-$Pr)_2$), 2.53 (t, 2 H, $^3J_{HH}$ = 6.9 Hz, $NCH_2CH_2NH_2$), 1.82 (s, 4 H, NH and NH_2), 1.05 (d, 12 H, $^3J_{HH}$ = 6.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR (D_2O, C_6D_6 added to the D_2O as the reference) δ 55.02 ($NCH_2CH_2NH_2$), 52.18 ($N(CH_2CH_2NH$-*i*-$Pr)_2$), 48.71 (CH), 42.66 (*i*-$PrNCH_2$), 37.68 (H_2NCH_2), 20.48 (CH_3). Attempts to isolate *i*-Pr_2-tren by ether extraction of a basic aqueous solution of the NaI adduct failed. Thus the NaI adduct of *i*-Pr_2-tren was vacuum distilled at 70−76 °C at 5 mTorr to give a light yellow oil in overall 15% yield (based on tren): ^1H NMR (C_6D_6) δ 2.70 (septet, 1 H, $^3J_{HH}$ = 6.3 Hz, CH), 2.57 (t, 2 H, $^3J_{HH}$ = 6.3 Hz, H_2NCH_2), 2.55 (t, 4 H, $^3J_{HH}$ = 6.0 Hz, *i*-$PrNCH_2$), 2.41 (t, 4 H, $^3J_{HH}$ = 6.0 Hz, $N(CH_2CH_2NH$-*i*-$Pr)_2$), 2.28 (t, 2 H, $^3J_{HH}$ = 6.3 Hz, $NCH_2CH_2NH_2$), 1.89 (s, 4 H, NH and NH_2), 1.05 (d, 12 H, $^3J_{HH}$ = 6.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 57.85 ($NCH_2CH_2NH_2$), 54.90 ($N(CH_2CH_2NH$-*i*-$Pr)_2$), 49.16 (CH), 45.82 (*i*-$PrNHCH_2$), 40.48 (NH_2CH_2), 23.47 (CH_3); MS(EI) *m/z* (ion, relative intensity), 231 ($M + H^+$, 11), 200 ($M - 2CH_3^+$, 4), 158 ($M - CH_2NH$-*i*-Pr^+, 33), 154 (10), 146 (13), 142 (5), 141 (11), 129 (8), 127 (19), 115 (5), 113 (6), 101 (32), 100 (25), 99 (49), 98 (6), 87 (33), 86 (CH_2CH_2NH-*i*-Pr^+, 61), 85 (18), 84 (8), 74 (5), 73 (5), 72 (CH_2NH-*i*-Pr^+, 33), 71 (7), 70 (17), 58 (32), 56 (15), 44 ($H_2NCH_2CH_2^+$ or $H_2NCHCH_3^+$, 100), 43 (*i*-Pr^+, 20), 42 (14), 41 (8); CIMS *m/z* (ion, relative intensity) 231 ($M + H^+$, 100); IR (neat between NaCl plates) 3356 m and 3284 m (ν(NH)).

Dimer 13. A solution of $Ti(NMe_2)_4$ (1.078 g, 4.808 mmol) in 15 mL of THF was added to a stirred solution of *i*-Pr_2-tren (1.108 g, 4.809 mmol) in 10 mL of THF. The initially yellow solution immediately turned red. The mixture was stirred at room temperature for 2 days after which the volatile components were removed *in vacuo* to give a red oily product. ^1H NMR spectra of the crude product in C_6D_6 revealed that it contained *i*-Pr_2-tren and **13** in an approximate ratio of 1:10. After addition of 7 mL of pentane to the crude product, an orange precipitate was obtained, which was filtered out, washed copiously with pentane, and dried *in vacuo* to give 0.38 g of product. A second crop of **13** (0.20 g) was obtained as red-orange crystals from a concentrate of the combination of the filtrate and the washings. The overall yield was 44%: mp: (dec) >230 °C; ^1H NMR (C_6D_6) δ 4.47 (t, 2 H, $^3J_{HH}$ = 5.7 Hz, H_g (for proton and carbon subscript labels, see the structural depiction in the Introduction), 4.00 (qq, 2 H, $^3J_{HH}$ = 6.6 Hz, H_f), 3.31 (dd, 4 H, $^3J_{HH}$ = 5.6 Hz, H_e), 2.58 (m, 4 H, $^3J_{HH}$ = 5.6 Hz, H_d), 2.35 (t, 2 H, $^3J_{HH}$ = 5.7 Hz, H_c), 1.40 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, H_b), 1.36 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, H_a); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 60.74 (C_g), 56.11 (C_c), 54.91 (C_f), 52.64 (C_d), 49.23 (C_e), 24.22 (C_a), 24.08 (C_b); LRMS (EI) *m/z* (ion, relative intensity), 548 (M^+, 7), 533 ($M - CH_3^+$, 3); HRMS (EI) calcd for $C_{24}H_{52}N_8Ti_2$ (M+) *m/z* 548.32739, found 548.32745, error 0.12 ppm; IR (KBr) no ν(NH) (4000−3000 cm^{-1}).

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Table 1. Crystallographic Data for **1**

formula	$C_{11}H_{27}N_5Ti$
fw	277.3
cryst size (mm)	0.50 × 0.50 × 0.25
cryst system	monoclinic
space group	$P2_{1/c}$
a (Å)	7.9550(7)
b (Å)	10.546(2)
c (Å)	18.105(2)
β (deg)	97.365(8)
V (Å$^{3)}$	1506.4(3)
Z	4
d_{calcd} (g/cm^3)	1.223
μ (mm^{-1})	4.719
λ(Cu Kα) (Å)	1.541 78
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0003F^2$
final R indices (obsd data)	$R^a = 0.0373$, $R_w{}^b = 0.0549$
R indices (all data)	$R^a = 0.0396$, $R_w{}^b = 0.0554$
goodness-of-fit[c]	1.75

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum(w^{1/2}(|F_o| - |F_c|))/\sum(w^{1/2}|F_o|)$; $w = 1/\sigma^2|F_o|$. [c] Goodness-of-fit $= (\sum(w(|F_o| - |F_c|)^2)/(m - n))^{1/2}$.

Attempted Reaction of 13 with NH_3. Method A. NH_3 gas, which had been passed through KOH pellets, was bubbled through a solution of **13** in toluene-d_8. The color of the solution faded from red-orange to yellow to colorless with time and a yellow-orange precipitate formed. Attempts to characterize the precipitate were not successful due to its insolubility in a variety of organic solvents, including DMSO-d_6.

Method B: NH_3 gas (0.66 mL at room temperature and atmospheric pressure, 2.7×10^{-5} mol), which had been generated from a blue liquid-NH_3/Na solution, was added to a solution of **13** (0.0074 g, 1.35×10^{-5} mol) in 0.5 mL of C_6D_6. The intensity of the methyl proton resonances for the free ligand *i*-Pr_2-tren increased with time.

Method C: NH_3 gas (3.81 mL at room temperature and atmospheric pressure, 5.68×10^{-5} mol), which had been generated from a blue liquid-NH_3/Na solution, was added to a stirred solution of **13** (0.043 g, 7.8×10^{-5} mol) in 3 mL of toluene. The mixture was stirred at room temperature for 3.5 days. The color of the solution changed from red-orange to yellow to colorless, and a yellow precipitate formed. The volatile components were removed *in vacuo* to give a yellow compound, which was insoluble in a variety of organic solvents.

Single Crystal X-ray Diffraction Study of 1. A crystal of **1** was attached to the tip of a glass fiber and mounted on a Siemens P4RA diffractometer for data collection at 213 ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the 40.0−50.0° 2θ range. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was also applied to the data. A series of azimuthal reflections was collected for the sample, and a semi-empirical absorption correction based on the azimuthal scans was applied to the data.

The space group $P2_1/c$ was chosen based on systematic absences. This assumption proved to be correct as determined by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the *E*-map. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were placed with C−H distances of 0.96 Å, and the methylene hydrogen atoms were refined as riding atoms with individual isotropic displacement parameters. The hydrogens of the methyl groups were initially refined as rigid groups in order to find their best torsional position, and then they were converted to riding atoms analogously to the hydrogens of the methylene groups.

Data collection and the structure solution were done at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-Plus programs.[18] Crystal, data collection, and refinement parameters are summarized in Table 1. Positional parameters are collected in Table 2, and selected bond distances and angles are listed in Table 3.

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

atom	x	y	z	$U_{\text{eq}}{}^a$
Ti	1643(1)	1776(1)	1322(1)	19(1)
N(1)	−188(3)	506(2)	1828(1)	26(1)
C(1)	−1617(4)	1285(3)	1998(2)	37(1)
C(2)	−2104(3)	2177(3)	1352(2)	31(1)
N(2)	−571(3)	2591(2)	1063(1)	23(1)
C(3)	789(4)	−48(3)	2501(2)	39(1)
C(4)	1867(4)	987(3)	2906(2)	38(1)
N(3)	2639(3)	1746(2)	2362(1)	29(1)
C(5)	−713(4)	−451(3)	1243(2)	37(1)
C(6)	823(4)	−909(3)	915(2)	34(1)
N(4)	1966(3)	151(2)	858(1)	25(1)
C(7)	−979(4)	3592(3)	519(2)	32(1)
C(8)	4161(4)	2362(3)	2708(2)	44(1)
C(9)	3624(4)	−278(3)	727(2)	43(1)
N(5)	2997(3)	2934(2)	830(1)	27(1)
C(10)	3299(5)	4206(3)	1126(2)	45(1)
C(11)	3465(4)	2849(3)	81(2)	41(1)

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

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

Bond Lengths			
Ti−N(1)	2.257(2)	Ti−N(2)	1.961(2)
Ti−N(3)	1.947(2)	Ti−N(4)	1.940(2)
Ti−N(5)	1.921(2)		
Bond Angles			
N(1)−Ti−N(2)	75.6(1)	N(1)−Ti−N(3)	78.6(1)
N(2)−Ti−N(3)	118.7(1)	N(1)−Ti−N(4)	77.2(1)
N(2)−Ti−N(4)	116.6(1)	N(3)−Ti−N(4)	110.1(1)
N(1)−Ti−N(5)	174.0(1)	N(2)−Ti−N(5)	98.7(1)
N(3)−Ti−N(5)	106.0(1)	N(4)−Ti−N(5)	104.3(1)

Attempted Solution of the Crystal Structure for 13. Several crystals of **13** were mounted on a Siemens P4RA at both 213 and 298 K. The samples were indexed by a set of up to 15 reflections chosen from a 360° rotation photograph. None of the specimens diffracted well. The unit cell at 298 K was orthorhombic, a = 8.701 Å, b = 17.044 Å, c = 20.304 Å, and V = 3011.01 Å^3. Axial photographs did verify an orthorhombic lattice, but they also revealed modulation and a possible superstructure along the *b*-axis. Further attempts to solve the structure were not made.

Results and Discussion

Syntheses. Although compound **1** was synthesized previously,[11a] it contained small amounts of unknown impurities as determined by its ^{1}H and ^{13}C{^{1}H} NMR spectra. Further purification of **1** was accomplished by separating the oily material from the high proportion of solidified product which formed when we carried out our earlier preparation. Using filter paper to absorb the oil followed by sublimation of the crude solid, and recrystallization of the sublimate from pentane, a 52% overall yield of **1** was obtained.

An attempt to prepare **9** was carried out by the direct reaction of tren with $TiCl_4(THF)_2$ in the presence of a base (reaction 1).

$$\text{xsEt}_3\text{N} + (\text{H}_2\text{NCH}_2\text{CH}_2)_3\text{N} + \text{TiCl}_4(\text{THF})_2 \xrightarrow[\text{THF}]{} 3\,\text{Et}_3\text{NHCl} + (\mathbf{9})_x + \text{Et}_3\text{N} \quad (1)$$

The ^{1}H NMR spectrum of the crude product in DMSO-d_6 revealed the presence of Et_3NHCl, which could be washed out by warm acetonitrile. However, the final product could not be sublimed; it is insoluble in a variety of organic solvents and it is only partly soluble in DMSO, indicating the formation of polymer or oligomer of **9**.

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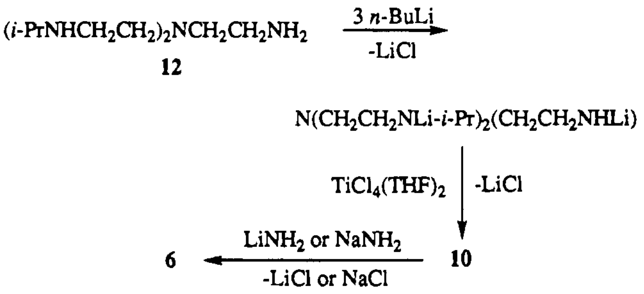
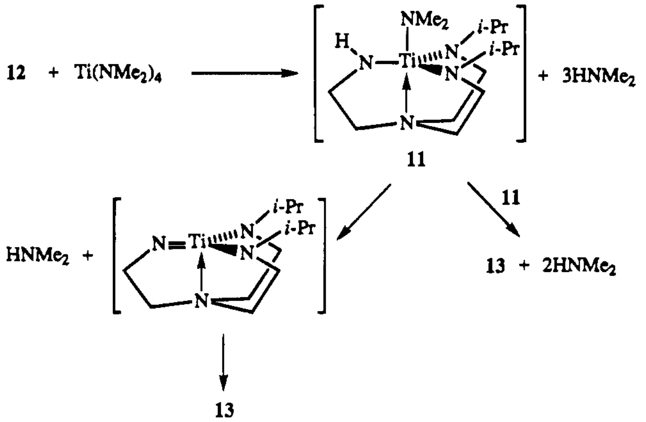
(18) SHELXTL-Plus, Siemens Analytic X-ray, Inc., Madison, WI.

Scheme 1



Scheme 2



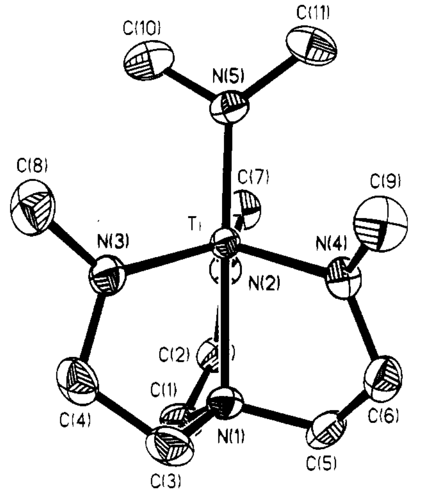
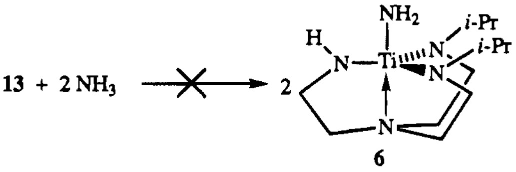


Figure 1. Molecular structure of **1**. The ellipsoids are drawn at the 50% probability level.

Although *i*-Pr$_3$-tren could be synthesized as a major product at elevated temperature,[17] a higher proportion of *i*-Pr$_2$-tren is generated at lower temperature (see Experimental). The isolation of *i*-Pr$_3$-tren from *i*-Pr$_2$-tren was achieved by the reaction of the mixture with NaI, in which *i*-Pr$_2$-tren preferentially forms an adduct with the NaI.[17] In the present paper we confirm the presence of *i*-Pr$_2$-tren (**12**) in the adduct by both ^{1}H and ^{13}C-{^{1}H} NMR spectra in D$_2$O and obtain **12** in 15% yield (based on tren) by vacuum distillation of its solid NaI adduct. Characterization of **12** was accomplished by ^{1}H and ^{13}C{^{1}H} NMR and mass spectral analysis.

Compound **10** was chosen as a starting material for the attempted synthesis of **6**, as shown in Scheme 1. Although similar reactions were successfully utilized to synthesize chlorotitanium-trisubstituted-tren complexes,[19,20] we were unable to obtain **10** in this way and managed only to produce a mixture of unknown (oligomeric) compounds that exhibited over 40 carbon resonances (probably via HCl elimination from **10** or a precursor to it). This led us to consider synthesizing the analogue **11** which we thought might be more stable to elimination (i.e., of HNMe$_2$). However, the novel compound **13** was obtained, as shown upon NMR and mass spectral analysis. Unfortunately repeated elemental analyses for this complex were unsatisfactory, owing to its extreme air- and moisture-sensitivity. Attempts to synthesize a zirconium analogue by an analogous method has not been successful so far. A possible pathway for the formation of **13** may involve intermediate **11**, formed via transamination, which is not stable because of the presence of an active amido-nitrogen proton which attacks the NMe$_2$ group allowing **13** to form with accompanying elimination of HNMe$_2$. The latter process could occur via sequential nucleophilic attack of an amido nitrogen on the Ti of a second molecule of **11** or by a prior HNMe$_2$ elimination and intermolecular coupling process as indicated in Scheme 2. Partial evidence for this pathway is the observation that the ^{1}H NMR spectrum of an aliquot of the crude reaction mixture taken after 5 h of reaction time showed a new resonance at 3.34 ppm for an NMe$_2$ group and two new doublets at 1.26 and 1.22 ppm, respectively, for the *i*-Pr methyl proton resonances attributable to intermediate **11**. These peaks (which were of low intensity) disappeared after 48 h of reaction time. Attempts to produce **6** by the reaction of **13** with ammonia as shown in reaction 2 failed, owing to the formation of what



(2)

appear to be polymeric products. Thus it is reasonable to assume that all the desired compounds **5-8** are unstable, due to the presence of an active proton on amido nitrogen and the possibility of NH$_3$ evolution and subsequent polymerization.

Crystal Structure of 1. The molecular structure of monomeric azatitanatrane **1** shown in Figure 1 features a central titanium atom in a slightly distorted TBP coordination environment. The molecule exhibits virtual C_s symmetry with the mirror plane passing through the N(1)$-$Ti$-$N(5) atoms and the C(1)$-$C(2)$-$N(2) arm. The N(1)$-$Ti$-$N(5) angle in **1** is not quite linear (174.0(1)°). The titanium atom is displaced from the plane formed by the three equatorial nitrogen atoms by 0.436 Å (sum of angles = 345.4(3)°) in the direction of the Me$_2$N group. It is interesting to note that the geometries around the equatorial nitrogens (average sum of angles = 358.1(3)°) and the axial Me$_2$N nitrogen (sum of angles = 358.3(2)°) are virtually the same, suggesting nearly equal π-donating opportunities for the two types of nitrogens to the titanium.

Often, axial bonds in TBP structures are longer than when the same linkage is in the equatorial position. This can be seen, for example, in the structures of **14**$-$**16**.[21] However, axial bonds that are equal to or shorter than their equatorial counterparts are also reported, as was seen in the structures of **17**[22] and **18**,[23] respectively. In **1** the Me$_2$N$-$Ti bond length (1.921(2) Å) is

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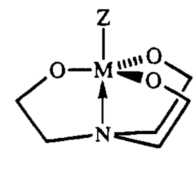
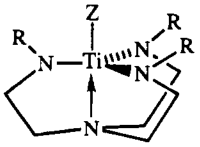
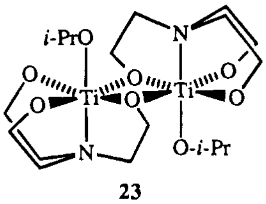


	M	Z
14	Si	EtO
15	Si	Me$_2$O
16	Si	EtO···HO$_2$CCF$_3$
17	Ti	Ph$_3$SiO
18	Ti	1/2 OCMe$_2$CMe$_2$O

shorter than the average Ti–N$_{eq}$ distance (1.949 (2) Å). Yet the Ti–N$_{eq}$ distance in **1** is not unusually short since it is within experimental error of the average Ti–N$_{eq}$ bond length for **19** (1.939(4) Å[11b]) and **20** (1.924(8) Å[20]), slightly longer than that in **21** (1.920(6) Å[20]), and longer than that for **22** (1.901(9) Å[20,24]). Moreover, the Me$_2$N–Ti distance is shorter than the lower limit of the average for titanium amide complexes (mean distance = 1.939 Å[25]). Interestingly, the transannular Ti–N$_{ax}$ distance (2.257 (2) Å) in **1** is also abnormally short since it is shorter than the lower limit of the average distance observed for Ti-coordinated tertiary amines (mean distance = 2.296 Å[25]). The Ti–N$_{ax}$ bond length in **1** is within experimental error of that for **17** (2.264(3) Å[22]) and **20** (2.227(11) Å[20]), somewhat longer than that reported for **21** (2.229(6) Å[20]), and considerably longer than that in **22** (2.209(9) Å[20,24]). The Ti–N$_{ax}$ bond in **1** is shorter than that in **18** (2.282(3) Å[23] despite the greater electronegativity of the oxygens in **18**) and in **19** (2.451(5) Å[11b] which may be due to the steric demands of the SiMe$_3$ groups). The Ti–N$_{ax}$ bond length in **1** is also shorter than those in the titanatrane dimers **23**[26] (2.333 (1) Å and **24**[11a] (2.270 (2) Å).



	R	Z
19	SiMe$_3$	OSiMe$_3$
20	Me	Cl
21	*i*-Pr	Cl
22	Et	O$_3$SCF$_3$



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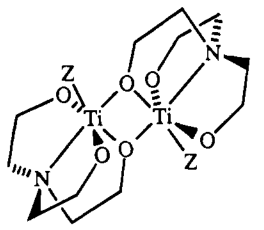


24 (Z = NMe$_2$)

This may be attributable to the electron density enhancement of the titanium owing to the expansion of its coordination number to 6. It was found by comparing the pairs of structures **17**, **18** and **23**, **24** that in each case the compound with the shorter Ti–N$_{ax}$ bond has a longer Ti–O bond distance trans to this bond.[11a,22,23] By contrast the rather short Ti–N$_{ax}$ bond in **1** does not seem to lengthen the Ti–N bond trans to it.

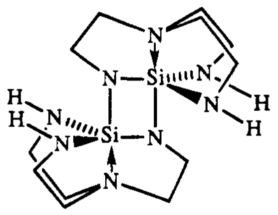
NMR Spectra. Solution ^{1}H and ^{13}C NMR spectra of azatitanatrane **1** exhibited characteristics of monomeric behavior. As is typical for azametallatranes,[11,13,19,20,27] the methylene protons of **1** constitute an AA'XX' spin system showing two virtual triplets in their ^{1}H NMR spectrum at room temperature in solution, as expected for virtual C_{3v} symmetry. The overall symmetry in the solid state of **1** is C_s owing to the two-fold symmetry of the axial NMe$_2$ group. However, C_{3v} symmetry is expected in solution at room temperature on the NMR time scale owing to rapid rotation of the NMe$_2$ group. Similar behavior was observed for the tin analogue of **1**.[27]

Table 4. Correlation of ^{1}H and ^{13}C NMR Chemical Shifts for **13**

δ(^{13}C) (ppm)	δ(^{1}H) (ppm), assgnt[a]	carbon atom[a]
	Methyl Groups	
24.08	1.40, H_b	C_b
24.22	1.36, H_a	C_a
	Methylene Groups	
49.23	3.31, H_e	C_e
52.64	2.58, H_d	C_d
56.11	2.35, H_c	C_c
60.74	4.47, H_g	C_g
	Methine Groups	
54.91	4.00, H_f	C_f

[a] For atom-labeling scheme, see structure for **13** in the Introduction.

In contrast to the simple appearance of the ^{1}H and ^{13}C{^{1}H} spectra of compound **1** in the methylene region, four signals in both the ^{1}H and ^{13}C{^{1}H} NMR spectra for the methylene groups were observed in the case of **13**, reflecting its dimeric nature. The two methyl groups in each isopropyl substituent exhibited two doublets and two singlets in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively, indicating the diasterotopic nature of the isopropyl groups. Support for the dimeric structure of **13** stems from similar spectra observed for the silicon compound **25** (which has been structurally determined by single-crystal X-ray diffraction)[28] except that the latter compound shows two multiplets for the methylene proton resonances of the nonbridging amido arms while **13** exhibits a multiplet (H$_d$) and one doublet of doublets (H$_e$) due to isochronous resonances in the four-spin system (see later).



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The assignment of the signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **13** is based on integration, couplings in the ^{1}H NMR, ^{1}H^{13}C heterocorrelated NMR, and ^{1}H^{1}H NOESY spectra. Cross peaks in the ^{1}H^{13}C heterocorrelated 2D spectrum of **13** reveal the connectivities between the carbon and the proton signals (Table 4), in which each proton signal corresponds to a carbon resonance. However, it is difficult to assign specifically the signals of the methylene groups for both the ^{1}H and the ^{13}C{^{1}H} spectra. Therefore, a 2D ^{1}H^{1}H NOESY experiment was carried out. From these spectra (see Figure 2), the following coupling relationship can be observed:

a, b $\longleftrightarrow$ e
a, b $\longleftrightarrow$ f
a, b $\longleftrightarrow$ g
c $\longleftrightarrow$ d
c $\longleftrightarrow$ e

c $\longleftrightarrow$ g
d $\longleftrightarrow$ e
d $\longleftrightarrow$ g
e $\longleftrightarrow$ f
f $\longleftrightarrow$ g

From the observed through-space couplings a,b $\leftrightarrow$ e and e $\leftrightarrow$ f, peak e can be unambiguously assigned as shown in the structure

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(24) The value reported in ref 20 is incorrect owing to a labeling error.

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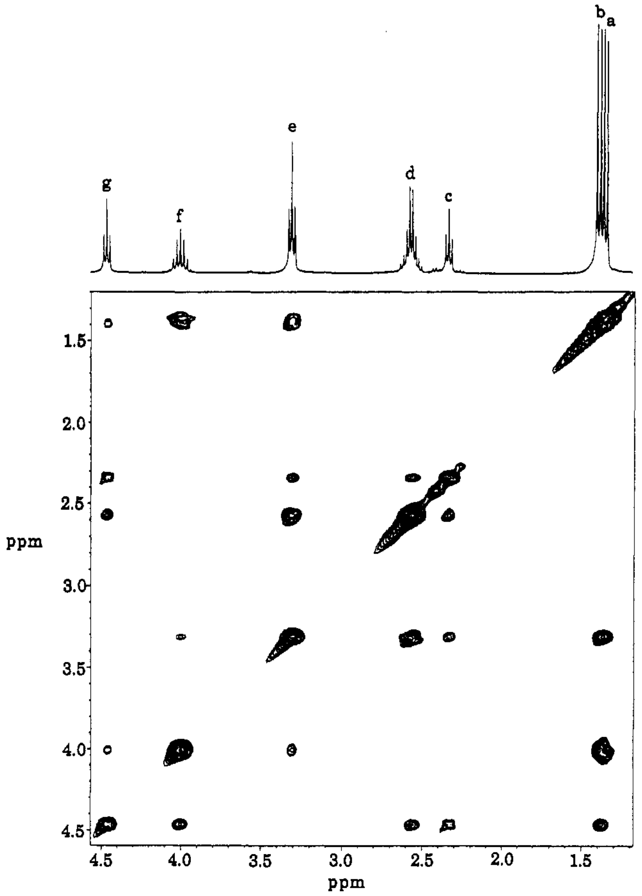

Figure 2. ^1H NMR spectrum of **13** in C_6D_6 (for labels see proposed structure **13** in the Introduction) and its unsymmetrized $^1H^1H$ NOESY 2D NMR spectrum.

proposed for **13** in the Introduction. Similarly, peak g is assigned based on the though-space couplings f ↔ g and a,b ↔ g. From selective decoupling ^1H NMR experiments, the remaining methylene proton signals can be assigned. The $^{13}C\{^1H\}$ NMR peaks of **13** can also be assigned from the $^1H^{13}C$ heterocorrelated experiment (Table 4).

On the basis of the proposed dimeric configuration of **13**, two types of d and two types of e proton resonances would be expected because of the presence of inner and outer methylene protons related to the mirror plane passing through the central Ti_2N_2 ring. Although a multiplet (eight lines) for the d proton resonances is seen in the spectrum in Figure 2 obtained on a 300 MHz spectrometer (probably owing to an AB system with additional coupling to e protons), only a doublet of doublets is observed for the e protons. This can be attributed to accidentally isochronous resonances for the two types of e protons which may be coupling equally to the two different d protons. This conclusion is confirmed by the ^1H NMR spectrum of **13** obtained at higher field (500 MHz), in which the same resonance patterns at the same chemical shifts and with the same coupling constants as those obtained at lower field (300 MHz) are observed, except that the signal for the d protons now shows a symmetrical multiplet with nine lines. It is noteworthy that both the proton and the carbon resonances for the methylene groups bound to the bridging amido nitrogens are deshielded by 1.90 and 20.26 ppm, respectively, relative to the corresponding signals for uncoordinated ligand **12** (see Experimental). This is probably due to the greatly reduced electron density on the bridging amido nitrogens occasioned by their coordination to two titanium metal centers. Interestingly, no exchange process was observed on the NMR time scale in the variable-temperature ^1H NMR spectra of **13** in toluene-d_8 from −78 to 100 °C, indicating a remarkably rigid structure in solution.

Conclusions. Azatitanatrane **13** arises from the transamination of $Ti(NMe_2)_4$ with the disubstituted tren ligand, **12**. Compound **13** possesses a dimeric structure as determined by ^1H, $^{13}C\{^1H\}$, and $^1H^1H$ NOESY NMR and mass spectroscopic techniques. Its structure is rigid in solution as judged by VT ^1H NMR spectroscopy. It seems likely that the monomeric compounds **5-11** may be impossible to synthesize by either transamination or metathesis reactions because of the presence of an active proton on an equatorial nitrogen, thus leading to easy elimination of HZ, with subsequent polymerization or oligomerization.

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Supporting Information Available: Text describing X-ray procedures, tables of crystal data, bond distances, bond angles, hydrogen atom positional and *U* parameters, and general displacement parameter expressions, and a packing diagram (10 pages). Ordering information is given on any current masthead page.

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