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Synthesis and Structures of N-Alkylated Azatitanatranes

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The N-alkylated azatitanatranes $N(CH_2CH_2NR)_3TiCl$ [R = Me (**1**), Et (**2**), *i*-Pr (**3**)] have been prepared and **1** and **3** structurally characterized by X-ray crystallography: **1**, orthorhombic, *Pmna*, $a = 11.293(3)$ Å, $b = 11.977(3)$ Å, $c = 9.722(3)$ Å, $V = 1314.96$ Å^3, $Z = 4$, $R = 0.0629$; **3**, cubic, *Pa*3, $a = 15.928(4)$ Å, $V = 4040.95$ Å^3, $Z = 8$, $R = 0.0792$. The halide ligand in **2** and **3** could be replaced by more labile ligands by chloride abstraction using the appropriate silver salts. A single-crystal X-ray structure analysis of $N(CH_2CH_2NEt)_3TiOSO_2CF_3$ (**4**), the first azatrane–triflate to be reported, was carried out. Crystal data for **4**: triclinic, $P\bar{1}$ (No. 2), $a = 16.039(4)$ Å, $b = 16.473(4)$ Å, $c = 8.954(3)$ Å, $\alpha = 105.75°$, $\beta = 106.17(2)°$, $\gamma = 107.54(2)°$, $V = 1996.33$ Å^3, $Z = 4$, $R = 0.0842$. The titanium amido complexes reported here may find use as building blocks in more complex structural arrays.

Introduction

Ligands derived from tris(2-aminoethyl)amine have recently found widespread application in the coordination chemistry of high-valent early transition metals.[1] As triamido ligands they ideally meet the electronic requirements of highly Lewis acidic metal centers.[2–4] Their "preconceived" coordination geometry effects the steric shielding of a large sector in the coordination sphere of these metals, leaving only a relatively small portion as "reactive center". The size and geometry of the latter may be systematically varied by the appropriate choice of the peripheral N-bonded substituents, the extreme case being the effective shielding of a vacant coordination site by means of very bulky silyl groups as shown recently by Schrock and co-workers.[5]

Azametallatranes of the transition metals have been synthesized by amine exchange reactions[2] and transmetallations[3] as well as salt methathesis reactions of the lithium amides with suitable transition metal complexes.[4] The hitherto most widely used ligand system in transition metal complexes is the trimethylsilylated tren derivative $\{N(CH_2CH_2NSiMe_3)_3\}^{3-}$ which, if coordinated to an early transition metal, was found to stabilize highly reactive molecular fragments such as phosphinidenes[6] and terminal selenides and tellurides.[7] Verkade and co-workers have recently published several titanium and vanadium complexes containing the methylated tren-derived ligand $\{N(CH_2CH_2NMe)_3\}^{3-}$.[2,3] This system offers a more open reactive site at the transition metal than the silylated species and therefore a chemical reactivity which is less constrained by the steric requirements of the N-bonded substituents. In our work with tripodal amido ligands,[8,9] we have found that the electronic properties of the transition metal amides are crucially dependent upon the nature of the α-substituents at the amido–nitrogen atoms which control the thermal stability and, most of all, the redox-chemistry of the metal complexes.[10,11] The latter is of particular interest for their application in subsequent metathetical condensation reactions yielding more complex metal–metal-bonded structural arrays.[12]

In continuation of our recent work on polydentate amides of tetravalent titanium we report the synthesis of a number of novel N-alkylated azatitanatranes and their solid-state structures along with their activation through substitution of the halide ligand by more labile groups.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Argon. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and dried over 4-Å molecular sieves.

The ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13 and 50.32 MHz, respectively) with tetramethylsilane and $CFCl_3$ as references. Infrared spectra were recorded on Perkin Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the Chemistry Department at Würzburg. Melting points were determined by differential thermal analysis (DTA) using a TA 9000 thermal analyzer by DuPont. $TiCl_4(THF)_2$,[13] $TiBr_4(THF)_2$,[13] and $N(CH_2CH_2NHMe)_3$[14] were prepared according to literature procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. The amines $N(CH_2CH_2NHEt)_3$ and $N(CH_2CH_2NH\text{-}i\text{-}Pr)_3$ were prepared by methods previously reported for related triamines.[8]

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N(CH$_2$CH$_2$NHEt)$_3$. Bp: 96 °C (0.2 Torr). ^{1}H-NMR ($\mathrm{CDCl_3}$, 295 K): δ = 1.04 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 7.1 Hz, $\mathrm{C}\mathit{H}_3$), 1.35 (s, $\mathrm{N}\mathit{H}$), 2.51 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.9 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 2.58 (m, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{CDCl_3}$, 295 K): δ = 14.8 ($\mathit{C}\mathrm{H_3}$), 43.6 ($\mathit{C}\mathrm{H_2CH_3}$), 47.1 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 53.9 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$). IR (neat): 3304 (m), 2960 (s), 2928 (s), 2888 (s), 2816 (m), 1456 (m), 1376 (m), 1136 (m), 1056 (m), 768 (m) cm^{-1}. Anal. Calcd for $\mathrm{C_{12}H_{30}N_4}$: C, 62.56; H, 13.12; N, 24.32. Found: C, 62.25; H, 13.71, N, 24.56.

N(CH$_2$CH$_2$NH-*i*-Pr)$_3$. Bp: 103 °C (0.2 Torr). ^{1}H-NMR ($\mathrm{CDCl_3}$, 295 K): δ = 0.93 (d, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.2 Hz, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 1.16 (s, $\mathrm{N}\mathit{H}$), 2.49 (m, $\mathrm{N(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{N)_3}$), 2.61 (sept, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{CDCl_3}$, 295 K): δ = 22.8 ($\mathit{C}\mathrm{H_3}$), 45.2 ($\mathit{C}\mathrm{H}$), 48.7 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 54.5 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N)_3}$). IR (neat): 3288 (m), 2960 (vs), 2892 (s), 2828 (s), 1664 (w), 1468 (s), 1380 (s), 1336 (m), 1180 (s), 1124 (m), 1052 (m), 740 (m) cm^{-1}. Anal. Calcd for $\mathrm{C_{15}H_{36}N_4}$: C, 66.12; H, 13.32; N, 20.56. Found: C, 65.83; H, 13.22, N, 20.77.

General Procedure for the Preparation of the Azatitanatranes 1–3. A 2.5 M solution of *n*-butyllithium in hexane (18.42 mL = 46.2 mmol) was slowly added to a stirred solution of tris(alkylaminoethyl)amine (15.4 mmol) in 100 mL of toluene, which was cooled at –50 °C. The reaction mixture was warmed to room temperature over a period of 30 min, subsequently stirred for another 2 h, and then cooled to –60 °C. To the lithium amide solution was added 5.34 g (16.00 mmol) of solid $\mathrm{TiCl_4(THF)_2}$; the reaction mixture was warmed to room temperature over a period of 4 h and stirred for 4 d. After evaporation of the solvent, extraction of the residue with 100 mL of pentane, and filtration through a G3-frit, the solution obtained was concentrated to ca. 30 mL and stored at –30 °C. The Ti complexes **1–3** precipitated as black crystalline solids which were isolated by filtration and subsequently dried *in vacuo*.

N[CH$_2$CH$_2$NMe]$_3$TiCl (1). Yield: 31%. Mp: 40 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 2.44 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.8 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.03 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 3.51 (s, $\mathrm{C}\mathit{H}_3$). $\{^1\mathrm{H}\}$ ^{13}C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 46.7 ($\mathit{C}\mathrm{H_3}$), 53.2 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 59.0 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$). IR (Nujol): 1460 (s), 1417 (w), 1378 (s), 1348 (w), 1263 (w), 1144 (m), 1043 (s), 1012 (m), 939 (w), 848 (m), 798 (w), 748 (w) cm^{-1}. Anal. Calcd for $\mathrm{C_9H_{21}N_4TiCl}$: C, 40.24; H, 7.88; N, 20.86. Found: C, 40.53; H, 7.74, N, 20.46.

N[CH$_2$CH$_2$NEt]$_3$TiCl (2). Yield: 47%. Mp: 44 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.17 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.9 Hz, $\mathrm{C}\mathit{H}_3$), 2.49 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.8 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.12 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 3.82 (q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 16.5 ($\mathit{C}\mathrm{H_3}$), 53.5 ($\mathit{C}\mathrm{H_2}$), 54.6 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 55.3 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$). IR (Nujol): 1466 (s), 1385 (m), 1373 (m), 1350 (m), 1303 (w), 1267 (w), 1187 (w), 1143 (w), 1122 (m), 1073 (m), 1052 (s), 1032 (m), 953 (w), 854 (m), 798 (w), 782 (w), 749 (m) cm^{-1}. Anal. Calcd. for $\mathrm{C_{12}H_{27}N_4TiCl}$: C, 46.39; H, 9.73; N, 18.03. Found: C, 46.68; H, 9.54, N, 17.55.

N[CH$_2$CH$_2$N-*i*-Pr]$_3$TiCl (3). Yield: 51%. Mp: 107 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.14 (d, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.6 Hz, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 2.46 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.0 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.10 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 5.28 (sept, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 22.0 ($\mathit{C}\mathrm{H_3}$), 47.1 ($\mathit{C}\mathrm{H}$), 53.5 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 56.2 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N)_3}$). IR (Nujol): 1461 (s), 1373 (s), 1261 (w), 1155 (w), 1068 (w), 1032 (w), 990 (w), 819 (w), 724 (w) cm^{-1}. Anal. Calcd for $\mathrm{C_{15}H_{33}N_4TiCl}$: C, 51.06; H, 9.43; N, 15.88. Found: C, 51.14; H, 9.75, N, 15.80.

General Procedure for the Chloride Abstraction and Substitution in 2 and 3. To a stirred solution of 1.41 mmol azatitanatrane chloride in toluene (30 mL), which was cooled at –50 °C, was added 1.48 mmol of solid silver salt (triflate or acetate). The reaction mixture was warmed to room temperature over a period of 4 h and subsequently stirred for another 1 h. After removal of the solvent *in vacuo*, extraction of the residue with pentane and filtration through a G3-frit, the filtrate was concentrated and stored at –30 °C to yield compounds **4–6** as black solids which were isolated by filtration and dried *in vacuo*.

N[CH$_2$CH$_2$NEt]$_3$Ti(OSO$_2$CF$_3$) (4). Yield: 35%. Mp: 32 °C dec. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.06 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 7.5 Hz, $\mathrm{CH_2C}\mathit{H}_3$), 2.40 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.2 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 2.95 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 3.51 (q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 16.3 ($\mathit{C}\mathrm{H_3}$), 50.9 ($\mathit{C}\mathrm{H_2}$), 54.1 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 54.9 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$), 120.3 ($\mathrm{CF_3}$, $^1J(^{19}\mathrm{F}{-}^{13}\mathrm{C})$ = 318 Hz). IR (Nujol): 1352 (s) 1260 (m), 1241 (m), 1201 (vs), 1167 (m), 1113 (m), 1069 (w), 1043 (m), 1005 (m), 945 (w), 916 (w), 848 (w), 795 (w), 734 (w), 638 (m) cm^{-1}. Anal. Calcd for $\mathrm{C_{13}H_{27}F_3N_4O_3TiS}$: C, 36.80; H, 6.41; N, 13.20. Found: C, 36.47; H, 6.55, N, 12.94.

N[CH$_2$CH$_2$N-*i*-Pr]$_3$Ti(OSO$_2$CF$_3$) (5). Yield: 48%. Mp: 83 °C dec. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.05 (d, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.4 Hz, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 2.41 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.0 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 2.96 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 4.71 (sept, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 21.9 ($\mathit{C}\mathrm{H_3}$), 46.7 ($\mathit{C}\mathrm{H}$), 52.7 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 54.3 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$), 121.2 ($\mathrm{CF_3}$, $^1J(^{19}\mathrm{F}{-}^{13}\mathrm{C})$ = 315 Hz). IR (Nujol): 1283 (m), 1262 (vs), 1201 (w), 1160 (m), 1072 (w), 1035 (s), 808 (m), 728 (s), 642 (s) cm^{-1}. Anal. Calcd for $\mathrm{C_{16}H_{33}F_3N_4O_3TiS}$: C, 41.21; H, 7.13; N, 12.01. Found: C, 41.41; H, 7.33, N, 11.94.

Table 1. Crystal Data and Experimental Details for **1**, **3**, and **4**

	1	**3**	**4**
empirical formula	$\mathrm{C_9H_{21}N_4ClTi}$	$\mathrm{C_{15}H_{33}N_4ClTi}$	$\mathrm{C_{13}H_{27}N_4F_3O_3STi}$
fw	268.65	352.81	424.34
cryst system	orthorhombic	cubic	triclinic
a (Å)	11.293(3)	15.928(4)	16.039(4)
b (Å)	11.977(3)	15.928(4)	16.473(4)
c (Å)	9.722(3)	15.928(4)	8.954(3)
α (deg)			105.75(2)
β (deg)			106.17(2)
γ (deg)			107.54(2)
V (Å^3)	1314.96	4040.95	1996.33
Z	4	8	4
D_{calcd} (g cm^{-1})	1.357	1.160	1.412
space group	*Pnma*	*Pa*3	$P\bar{1}$
*F*000	568	1520	888
μ(Mo-Kα) (cm^{-1})[a]	8.1	5.4	5.5
θ-range (deg)	3–25	3–25	3–25
no. of obsd. reflcns $I > 3\sigma(I)$[b]	616	431	2883
no. of variables[c]	62	64	365
residuals *R*; R_w	0.0629; 0.0676	0.0792; 0.0814	0.0842; 0.0935
data/param	9.90	6.73	7.90

[a] An empirical absorption correction, using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39* 158) was applied to all three crystals; the data were corrected for Lorentz and polarization effects. [b] The intensities of three representative reflections were measured every 5 h of X-ray exposure time; they remained constant throughout the data collection indicating in every case crystal and electronic stability (no decay correction was applied). [c] Neutral atom scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables of X-ray Crystallography*, The Kynoch Press: Birmingham, England, 1974.

N[CH$_2$CH$_2$NEt]$_3$Ti(O$_2$CCH$_3$) (6). Yield: 40%. Mp: 69 °C dec. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.13 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.9 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$), 2.04 (s, $\mathrm{C}\mathit{H}_3\mathrm{CO_2}$), 2.55 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.8 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.10 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 3.61 (q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 16.8 ($\mathit{C}\mathrm{H_3CH_2}$), 23.8 ($\mathit{C}\mathrm{H_3CO_2}$), 52.2 ($\mathit{C}\mathrm{H_2CH_3}$), 53.4 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 54.6 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$), 170.6 ($\mathrm{O_2}\mathit{C}\mathrm{CH_3}$). IR (Nujol): 1640 (m), 1405 (m), 1268 (s), 1183 (m), 1148 (m), 1112 (s), 1089 (s), 1042 (s), 1012 (s), 943 (m), 845 (m), 795 (s), 742 (s), 720 (m) cm^{-1}. Anal. Calcd for $\mathrm{C_{14}H_{30}N_4O_2Ti}$: C, 50.31; H, 9.04; N, 16.76. Found: C, 50.64; H, 8.88, N, 17.02.

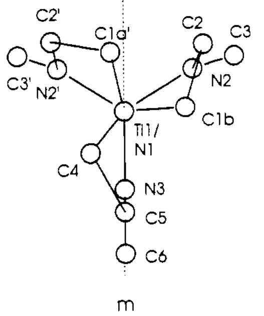
If solutions of either **4** or **5** were not handled with a rigorous exclusion of moisture, gradual conversion to the dimeric oxo–titanium complexes [N(CH$_2$CH$_2$NEt)$_3$Ti]$_2$O (**7**) and [N(CH$_2$CH$_2$N-*i*-Pr)$_3$Ti]$_2$O (**8**), respectively, occurred which precipitated reproducibility but in variable yields as red highly crystalline solids from the solutions.

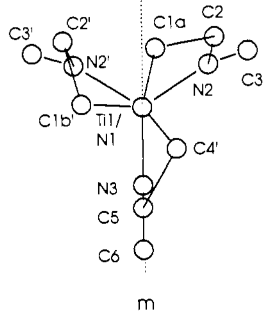
[N(CH$_2$CH$_2$NEt)$_3$Ti]$_2$O (7). ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.34 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.9 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$), 2.61 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.8 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.23 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 4.20 (q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 16.9 ($\mathit{C}\mathrm{H_3CH_2}$), 52.4 ($\mathit{C}\mathrm{H_2CH_3}$), 53.7 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 55.0 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$). Anal. Calcd for $\mathrm{C_{24}H_{54}N_8OTi_2}$: C, 50.88; H, 9.61; N, 19.78. Found: C, 50.64; H, 9.45, N, 20.02.

[N(CH$_2$CH$_2$N-*i*-Pr)$_3$Ti]$_2$O (8). ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 1.35 (d, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 6.4 Hz, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 2.58 (t, $^3J(^1\mathrm{H}{-}^1\mathrm{H})$ = 5.9 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_2N)_3}$), 3.22 (t, $\mathrm{N(CH_2C}\mathit{H}_2\mathrm{N)_3}$), 5.17 (sept, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$). $\{^1\mathrm{H}\}^{13}$C-NMR ($\mathrm{C_6D_6}$, 295 K): δ = 23.1 ($\mathit{C}\mathrm{H_3}$), 46.2 ($\mathit{C}\mathrm{H}$), 52.1 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_2N)_3}$), 55.9 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_2N)_3}$). Anal. Calcd for $\mathrm{C_{30}H_{66}N_8OTi_2}$: C, 55.38; H, 10.22; N, 17.22. Found: C, 55.10; H, 10.33, N, 16.94.

X-ray Crystallographic Study of 1, 3, and 4. The black crystals of compounds **1**, **3**, and **4** all had a block-shape prismatic habit. A regularly shaped crystal of **1** with the approximate dimensions 0.32 × 0.21 × 0.29 mm was mounted under argon in a Lindemann capillary; crystals of **3** and **4** with the approximate dimensions 0.40 × 0.40 × 0.51 mm and 0.40 × 0.24 × 0.32 mm, respectively, were mounted in a similar way. The X-ray diffraction data were collected by using a Philips PW 1100 diffractometer with graphite-monochromated Mo Kα σ radiation. Unit cell parameters were determined by a least squares analysis of 25 automatically centered reflections in the range 10° < θ < 15°. Data were collected at 295 K in the range θ = 3–25° with a scan width of 0.80° using technique described previously.[15] Details are presented in Table 1.

The data analysis and refinement were carried out with the programs of the SHELX 76 software package.[16] Systematic absences indicated that the space group of **1** is either *Pnma* or *Pn*2$_1$*a* (nonstandard setting of *Pna*2$_1$). The positions of the Ti and Cl atoms were located from a Patterson synthesis and correspond to one molecule in a general position in *Pn*2$_1$*a* or, alternatively, in a special position in *Pmna* with Ti and Cl atoms in the mirror plane. Attempts were made to refine the structure in both space groups and the most satisfactory result was obtained in the centrosymmetric space group *Pmna*. In this space group, the site symmetry of the Ti atom imposes a crystallographic mirror plane on the molecule. The position of the remaining atoms were located with some difficulty in subsequent difference-Fourier maps. Six atoms were on the mirror plane N1, Ti1, Cl1, C5, N3, and C6; the amide nitrogen atom N2 and the two carbon atoms C2 and C3 bonded to it refined satisfactorily indicating that the mirror relationship to the three atoms C2′, N2′, and C3′ generated by the mirror plane was correct. Problems were encountered with the carbon atoms linked to the amide nitrogen atom N1.





The first atom, C4, bonded to N1 and C5 (both of which are on the mirror plane), lay approximately 0.7 Å out of the mirror plane and was therefore assigned an occupancy factor of 0.5. This indicates to a 50/50 random distribution of the molecule with two different orientations of the three carbons about the amine nitrogen atom N1. In accordance to this model, two different sites were detected for the carbon bridging N1 and C2 separated by 0.5 Å (C1a nd C1b) and were included with a site occupancy factor of 0.5. All attempts to refine a model based on just one orientation of the molecule in the noncentrosymmetric space group proved unsatisfactory.

The crystal structure of **4** contains two independent molecules per equivalent position in the centrosymmetric space group P$\bar{1}$. Delauney reduction failed to reveal any unit cell of higher symmetry. The positions of the two Ti atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from subsequent difference-Fourier maps. Initial refinement showed very high thermal parameters for the six carbon atoms bonded to the two independent amine nitrogen atoms N1a and N1b. Examination of a difference-Fourier map calculated with a fine grid (without these atoms) allowed each of them to be resolved into two separate peaks. These were interpreted as due to a disorder of molecules with different orientations at the amine nitrogen, similar to the situation found for **1**. Satisfactory refinement was obtained with site occupancy factors of 0.7 and 0.3 for the atoms of the two components of the disorder. Very high thermal parameters for the fluorine atoms and relatively high thermal parameters of the methyl carbon atoms of the ethyl groups indicate some rotational disorder of these terminal atoms which could not be resolved in either case.

Results and Discussion

Synthesis and Characterization of N(CH$_2$CH$_2$NR)$_3$TiCl [R = Me (1), Et (2), *i*-Pr (3)]. The azatitanatranes N[CH$_2$CH$_2$NR]$_3$TiCl [R = Me (**1**), Et (**2**), *i*-Pr (**3**)] may be obtained by direct salt metathesis of the lithiated amine precursors with TiCl$_4$(THF)$_2$ in toluene. Although the investigation of the product mixture by ^{1}H-NMR spectroscopy indicated a conversion of at least 70–80% to the desired Ti-complexes, the isolation of pure, solid product was entirely dependent upon the crystallization of the azatranes from pentane. The moderate yields in which the Ti-complexes are obtained (ca. 30–50%) therefore do not reflect the actual course of the reaction. All three complexes may be destilled *in vacuo*; however, a certain degree of decomposition and thus contamination of the product makes this way of isolation less desirable.

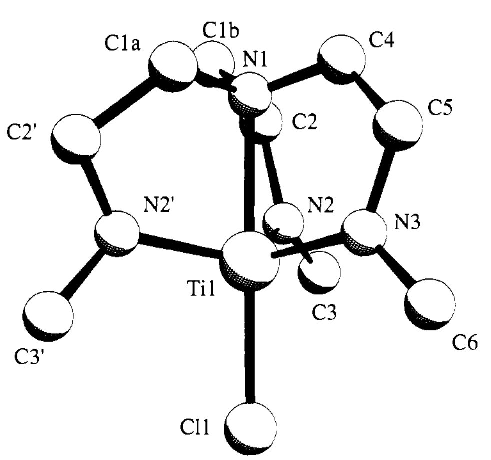


Figure 1. Molecular structure of N[CH$_2$CH$_2$NMe]$_3$TiCl (**1**).

The black, crystalline, moisture sensitive compounds **1**–**3** are soluble in all common aprotic organic solvents although they slowly decompose in halogenated hydrocarbons. Both the ^{1}H- and ^{13}C-NMR spectra are consistent with an overall 3-fold symmetry as would be expected for monomeric "azatrane" structures. In comparison to the free amine precursors, all signals in the ^{1}H- and ^{13}C-NMR spectra are shifted to lower field which is a consequence of the high Lewis acidity of the tetravalent titanium. The ^{1}H-NMR resonances of the methylene groups in the ligand framenwork of **1**–**3** appear as virtual triplets (representing virtual C_{3v} symmetry) at ambient temperature indicating rapid conformational exchange within these structural units, a feature noted previously by Verkade and co-workers in their investigation of the azatrane chemistry of pentavalent vanadium.[3]

The increasing steric demand of the amido ligand on going from **1** to **3** is reflected in an increased stability towards air and moisture. Whereas the isolation and handling of **1** requires extreme care, the isopropyl-substituted compound **3** is only moderately moisture sensitive.

Crystal Structures of 1 and 3. In order to establish the structural details of what is as yet an insufficiently studied class of transition metal complexes single-crystal X-ray structure analyses of both **1** and **3** were carried out. The molecular structure of **1** is depicted in Figure 1, the principal bond lengths and interbond angles are listed in Table 2, and the positional parameters are given in Table 3. Figure 2 shows the crystal structure of **3**, and the principal bond parameters are listed in Table 4 while the fractional coordinates are given in Table 5.

Compound **1** crystallizes in the orthorhombic space group *Pnma*. Its molecular structure in the crystal may be viewed as having a distorted trigonal bipyramidal coordination geometry with an overall idealized C_3-symmetry. The idealized molecular C_3-axis is defined by the atoms Ti, Cl, and the trans-annular nitrogen atom N1 which have an interbond angle deviating by 3.2° from the ideal value of 180°, a situation which is probably due to crystal packing effects. A consequence of the distorted geometry in the crystal is the variation of the related bond parameters within the tricyclic azatrane structure of the molecule (Table 2). The three five-membered rings adopt an envelope conformation similar to all the previously investigated monomeric

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Table 2. Principal Bond Lengths (Å) and Interbond Angles (deg) for **1**

Ti1–Cl1	2.292(4)	Ti1–N1	2.227(11)
Ti1–N3	1.927(9)	Ti1–N2	1.921(7)
N1–C4	1.456(25)	N1–C1a	1.492(24)
N1–C1b	1.45(3)	N3–C5	1.446(18)
N3–C6	1.408(16)	N2–C2	1.447(15)
N2–C3	1.430(13)	C2–C1a	1.69(3)
C2–C1b	1.54(3)	C4–C5	1.68(3)
N1–Ti1–Cl1	176.8(3)	N3–Ti1–Cl1	105.1(3)
N3–Ti1–N1	78.1(4)	N2–Ti1–Cl1	102.2(2)
N2–Ti1–N1	76.3(3)	N2–Ti1–N3	112.8(3)
C4–N1–Ti1	108(1)	C1a–N1–Ti1	111(1)
C1a–N1–C4	141(1)	C1b–N1–Ti1	107(1)
C1b–N1–C4	115(2)	C5–N3–Ti1	120.6(9)
C6–N3–Ti1	126.4(9)	C6–N3–C5	113(1)
C2–N2–Ti1	122.3(7)	C3–N2–Ti1	123.4(6)
C3–N2–C2	113.6(9)	N2–Ti1–N2	119.3(5)
C1a–C2–N2	109(1)	C1b–C2–N2	105(1)
C5–C4–N1	99(1)	C4–C5–N3	106(1)
C2–C1a–N1	96(1)	C1b–C1a–N1	59(1)
C2–C1b–N1	105(2)		

Table 3. Fractional Atomic Coordinates of **1**

atom	*x*	*y*	*z*
Ti1	0.26601(19)	0.25000	0.06885(19)
Cl1	0.1221(3)	0.2500	–0.0661(3)
N1	0.3977(10)	0.2500	0.2073(9)
N3	0.4137(8)	0.2500	–0.0117(9)
N2	0.2364(7)	0.4205(7)	0.1449(6)
C2	0.2980(11)	0.4586(16)	0.2462(10)
C3	0.1672(10)	0.5296(10)	0.0984(9)
C4	0.5004(20)	0.1717(23)	0.1704(17)
C5	0.5253(13)	0.2500	0.0475(14)
C6	0.4275(16)	0.2500	–0.1285(10)
C1a	0.3464(19)	0.3136(21)	0.3098(18)
C1b	0.4209(26)	0.3923(30)	0.2346(22)

azatranes (generating what Verkade has described as a "paddle wheel" arrangement).[1–7] The Ti atom at the center of the structure is displaced by 0.436 Å toward the chloride ligand with respect to the plane defined by the three nitrogen atoms N2–N4, a situation which leads to an average N(amide)–Ti–Cl angle of 103.1°. The bond length between the Ti atom and the axial amino–nitrogen atom is 2.227(11) Å and thus well within bonding distance of the metal atom and within the range of N(amine)–M bond lengths determined for the pentacoordinate monomeric complexes $N[CH_2CH_2NMe]_3V{=}O$ (*d*(V–N) = 2.321(6) Å),[3a] $N[CH_2CH_2NSiMe_3]_3VCl$ (*d*(V–N) = 2.238(6) Å)[4] and $N[CH_2CH_2O]_3TiOSiPh_3$ (*d*(Ti–N) = 2.264).[2] The average N(amide)–Ti bond length of 1.923 Å is comparable to that found in most Ti complexes containing chelating and nonchelating silyl amides,[17–19] and the Ti–Cl bond length of 2.292(4) is only slightly longer than the metal–Cl distance in $N(CH_2CH_2NSiMe_3)_3VCl$ (*d*(V–Cl) = 2.278(2) Å)[4] but well within the range found for other Ti–amido chlorides.[17,18]

Crystals of compound **3** have cubic space group symmetry (*Pa*3). The molecular axis coincides with a crystallographic 3-fold axis, and therefore, in contrast to the slightly distorted structure of **1**, the exact C_3-symmetry of the molecule is crystallographically imposed. The principal structural features of the azatrane cage are similar to those of **1** and thus do not require detailed discussion.

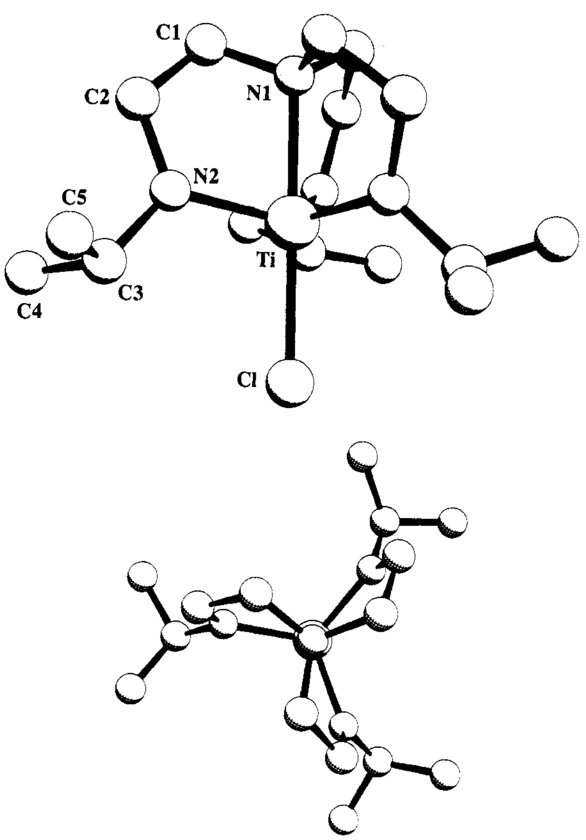

Figure 2. Top: (a) Molecular structure of $N[CH_2CH_2N\text{-}i\text{-}Pr]_3TiCl$ (**3**). Bottom: (b) View along the crystallographic 3-fold axis.

Table 4. Principal Bond Lengths (Å) and Interbond Angles (deg) for **3**

Ti–Cl	2.332(2)	Ti–N1	2.229(6)
Ti–N2	1.920(6)	N1–C1	1.441(10)
N2–C2	1.443(11)	N2–C3	1.496(12)
C1–C2	1.485(14)	C3–C4	1.501(14)
C3–C5	1.482(15)		
N1–Ti–Cl	180.0(1)	N2–Ti–Cl	103.6(2)
N2–Ti–N1	76.4(3)	C1–N1–Ti	107.1(5)
C2–N2–Ti	122.0(5)	C3–N2–Ti	121.8(5)
C3–N2–C2	115.9(7)	N2–Ti–N2	114.6(2)
N2–Ti–N2′	114.6(2)	C2–C1–N1	109.0(7)
C1–N1–C1′	111.7(8)	C1–N1–C1	111.7(8)
C1–C2–N2	110.2(7)	C4–C3–N2	111.3(7)
C5–C3–N2	112.8(8)	C5–C3–C4	111.1(9)

Table 5. Fractional Atomic Coordinates of **3**

atom	*x*	*y*	*z*
Ti	0.20389(8)	0.20389(8)	0.20389(8)
Cl	0.28841(12)	0.28841(12)	0.28841(12)
N1	0.1231(4)	0.1231(4)	0.1231(4)
N2	0.2621(4)	0.2019(4)	0.0984(4)
C1	0.1335(6)	0.1517(6)	0.0379(5)
C2	0.2236(6)	0.1700(6)	0.0228(6)
C3	0.3525(6)	0.2264(6)	0.0912(6)
C4	0.3635(6)	0.2998(7)	0.0331(6)
C5	0.4072(7)	0.1554(8)	0.0663(9)

Substitution of the Chloride Ligand in 2 and 3 by Oxygen Donor Ligands. The substitution of the chloride ligand in the azatitanatranes discussed here may be achieved by reaction with silver salts. Of particular interest in this context was the introduction of a triflate group, a ligand which previously has found application in the generation of substitutionally labile coordination sites.

Although reaction of **1** with Ag(OTf) [OTf = O_3SCF_3] at –50 °C in toluene leads to the gradual precipitation of AgCl and therefore probably to the desired product, the extreme lability of this species has thus far prevented its isolation and characteriza-

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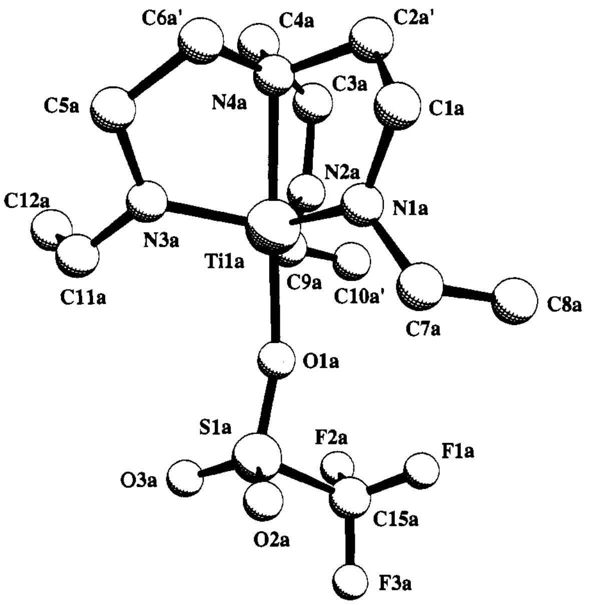

Figure 3. Molecular structure of "molecule 1" in the asymmetric unit of the unit cell of N[CH_2CH_2NEt]$_3$Ti(O_3SCF_3) (**4**). The basic structural features of the second molecule ("molecule 2") are essentially identical.

Table 6. Selected Bond Lengths (Å) and Interbond Angles (deg) of the Two Independent Molecules in **4**

	molecule A	molecule B
Ti1–N1	2.217(9)	2.200(9)
Ti1–N2	1.903(9)	1.887(9)
Ti1–N3	1.911(10)	1.894(10)
Ti1–N4	1.908(9)	1.903(9)
Ti1–O1	1.983(7)	1.991(7)
O1–S1	1.475(8)	1.460(7)
S1–C1s	1.762(21)	1.812(20)
N2–Ti1–N1	78.2(4)	78.5(4)
N3–Ti1–N1	79.3(4)	78.7(4)
N3–Ti1–N2	111.2(5)	110.6(4)
N4–Ti1–N1	75.8(4)	76.1(3)
N4–Ti1–N2	118.6(4)	119.1(4)
N4–Ti1–N3	117.0(5)	117.1(4)
O1–Ti1–N1	177.6(3)	178.2(4)
O1–Ti1–N2	103.3(4)	103.1(4)
O1–Ti1–N3	101.8(4)	101.5(4)
O1–Ti1–N4	101.8(4)	102.3(3)
S1–O1–Ti1	163.7(5)	164.1(6)
C1s–S1–O1	101.5(8)	102.2(7)

tion. On the other hand, the analogous triflate complexes derived from **2** and **3** were found to be sufficiently stable to allow complete characterization. Both N[CH_2CH_2NEt]$_3$Ti(OTf) (**4**) and N[CH_2CH_2N-*i*-Pr]$_3$Ti(OTf) (**5**) are obtained as purple-black crystalline solids which are soluble in hydrocarbons, indicating a nondissociative dissolution in these media. If moisture is not rigorously excluded, a slow hydrolytic conversion to the dinuclear oxo complexes [N(CH_2CH_2NEt)$_3$Ti]$_2$O (**6**) and [N(CH_2CH_2N-*i*-Pr)$_3$Ti]$_2$O (**7**) is observed. However, preliminary studies of the solutions of **4** and **5** in polar aprotic solvents such as THF indicate an at least partial dissociation of the triflate ligand. The chemistry of the highly electrophilic Ti complexes formed under these conditions is currently being investigated and will be reported elsewhere.[20] That the oxygen donor ligands are in general strongly bound to tetravalent Ti centers is substantiated by the relative inertness of the acetate complex N[CH_2CH_2NEt]$_3$Ti(OC(O)CH_3) (**8**) toward nucleophilic attack or dissociation in polar solvents.

The ^1H- and ^{13}C-NMR data of **4**–**8** are consistent with a similar effective molecular symmetry (C_{3v}) as those of **2** and **3**. The chemical shifts of the resonances of related nuclei in all Ti complexes reported here appear to be barely affected by the nature of the "axial" ligand provided that this position is occupied by an anionic ligand (halide or oxygen-donor ligand).

Table 7. Fractional Atomic Coordinates of the Two Independent Molecules of **4** in the Unit Cell[a]

atom	*x*	*y*	*z*
		Molecule A	
Ti1a	0.3253(1)	0.1184(1)	0.0836(2)
N1a	0.4119(7)	0.2303(6)	0.0281(11)
N2a	0.2359(7)	0.1660(6)	0.0006(11)
N3a	0.3494(8)	0.0482(7)	–0.0949(13)
N(4a)	0.4315(6)	0.1952(6)	0.2925(11)
O1a	0.2521(6)	0.0205(5)	0.1430(10)
S1a	0.1838(2)	–0.0348(2)	0.1957(5)
O2a	0.1942(11)	0.0129(8)	0.3591(15)
O3a	0.0918(7)	–0.0832(8)	0.0703(15)
F1a	0.3145(8)	–0.0855(11)	0.3033(26)
F2a	0.2097(12)	–0.1740(8)	0.0600(21)
F3a	0.1816(8)	–0.1735(7)	0.2745(17)
C1sa	0.2272(16)	–0.1191(15)	0.2174(27)
C1a	0.2661(11)	0.2532(11)	–0.0219(18)
C2a′	0.3806(15)	0.3038(15)	0.0536(28)
C3a	0.1353(10)	0.1113(10)	–0.0860(17)
C4a	0.0965(15)	0.0637(14)	–0.2730(22)
C5a	0.4033(11)	0.0921(11)	–0.1830(19)
C6a′	0.3985(16)	0.1895(15)	–0.1504(28)
C7a	0.2816(20)	–0.0492(17)	–0.2041(35)
C8a	0.3339(23)	–0.0968(20)	–0.1832(39)
C9a	0.5146(10)	0.2742(9)	0.3169(17)
C10a′	0.5165(16)	0.2629(15)	0.1373(27)
C11a	0.4447(9)	0.1746(9)	0.4502(15)
C12a	0.5078(11)	0.1234(11)	0.4739(20)
		Molecule B	
Ti1b	0.1750(1)	0.3818(1)	0.6402(2)
N1b	0.0884(7)	0.2722(6)	0.3871(11)
N2b	0.2635(7)	0.3350(6)	0.5974(12)
N3b	0.1516(8)	0.4519(6)	0.5096(12)
N4b	0.0689(6)	0.3054(6)	0.6664(10)
O1b	0.2496(5)	0.4804(5)	0.8709(9)
S1b	0.3158(2)	0.5346(2)	1.0464(4)
O2b	0.3037(10)	0.4864(8)	1.1530(13)
O3b	0.4089(7)	0.5856(8)	1.0650(15)
F1b	0.1856(8)	0.5862(11)	1.0786(21)
F2b	0.2896(11)	0.6748(8)	1.0284(17)
F3b	0.3194(8)	0.6745(8)	1.2652(13)
C1sb	0.2714(15)	0.6213(14)	1.1118(25)
C1b	0.2352(11)	0.2466(10)	0.4540(18)
C2b′	0.1190(16)	0.1979(16)	0.3711(27)
C3b	0.3641(10)	0.3889(9)	0.6684(17)
C4b	0.3983(13)	0.4322(12)	0.5608(23)
C5b	0.0987(12)	0.4102(11)	0.3246(20)
C6b′	0.0954(17)	0.3108(16)	0.2575(29)
C7b	0.2179(19)	0.5522(17)	0.5692(34)
C8b	0.1771(20)	0.6083(22)	0.5892(37)
C9b	–0.0151(10)	0.2249(10)	0.5281(18)
C10b′	–0.0165(18)	0.2355(17)	0.3590(30)
C11b	0.0560(8)	0.3244(8)	0.8292(14)
C12b	–0.0069(11)	0.3761(10)	0.8430(19)

[a] The disorder of the six carbon atoms (C2a, C6a, C10a, C2b, C6b, C10b) could be resolved. Only one of the respective two positions assigned to these atoms is given here.

Crystal Structure of N[CH_2CH_2NEt]$_3$Ti(OTf) (4). With the exception of the structures of $Cp_2Ti(OTf)_2$ and $Cp_2Ti(OTf)$(THF) reported by Thewalt and co-workers[21,22] we are not aware of structural investigations of Ti–triflato complexes by X-ray crystallography. Structures of amido–triflato complexes, in particular, have not been reported to date. In view of the properties of compounds **4** and **5** described in the previous section a fairly strong binding of the triflate anion to the Ti center was assumed. In order to get a detailed picture of the molecular geometry of these compounds, a single-crystal X-ray structure

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analysis of **4** was carried out. The molecular structure of **4** in the crystal is depicted in Figure 3, the principal bond parameters are listed in Table 6, and the fractional coordinates are given in Table 7.

The triclinic ($P\bar{1}$) crystals of **4** have two molecules in the asymmetric unit, one of which is shown in Figure 3. The overall structure again may be described as distorted trigonal bipyramidal with the amine-N atom and the triflate ligand occupying the apical positions. The three carbon atoms bonded to the apical N atom (in both molecules of the asymmetric unit) are disordered between the two possible positions of an overall "paddle wheel" arrangement of the azatrane ligand. Two of the peripheral ethyl groups are oriented almost parallel to the S1–C15 bond in the triflate unit. The bond distances and interbond angles within the ligand cage are similar to those found for **1** and **3**, indicating that the coordinated triflate ligand does not alter the geometry of the remaining part of the coordination sphere. The interbond angle between the two axial positions N4–Ti1–O1 is 177.6(4)° [178.2(4)°] [The bond parameters of the second independent molecule are given in brackets] and therefore close to the idealized value of 180° in a trigonal bipyramid. The S1–O1–Ti1 angle of 163.7(5)° [164.1(6)°] indicates a certain degree of π-character of the Ti–O(triflate) bond. The Ti–O bond length of 1.983(7) Å [1.991(7) Å] is close to that found in $Cp_2Ti(OTf)_2$ [d_{av}(Ti–O) = 2.004 Å][21] but somewhat longer than the Ti–O distances observed in most titanium alkoxides.[23]

Conclusions

The synthesis of **1**–**3** has shown that salt metathesis reactions of lithiated tren derivatives with titanium halide complexes provide a relatively universal preparative entry to the chemistry of azatitanatranes provided that the reaction conditions are chosen so as to suppress competing redox reactions. Subsequent replacement of the remaining halide ligand may be conveniently achieved by reaction with silver salts, and the compounds thus derived may find use in more elaborate transformations. The structural characterization of three azatitanatranes by X-ray crystallography has established the significant features of this class of coordination compounds.

We are currently studying the suitability of the azatrane derivatives as building blocks for the synthesis of more complex metal–metal bonded oligonuclear compounds, an effort which supplements the recently achieved stabilization of such species by use of polydentate amido ligands at the early transition metal.[12]

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Supplementary Material Available: Tables of the positional and thermal parameters and interatomic distances and angles for **1**, **3**, and **4** and drawings of molecules A and B for **4** (32 pages). Ordering information is given on any current masthead page.

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