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Monomeric and Dimeric Titanatranes

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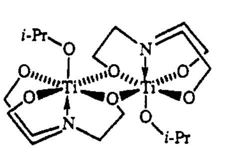
The synthesis and characterization of four new titanatranes $Z\text{-}Ti(OCH_2CH_2)_3N$ (Z = O-*t*-Bu (**5**), OPh (**6**), O_2CMe (**7**), NMe_2 (**8**) are reported. An X-ray crystal structure determination of **7** reveals a novel dimeric structure in which each titanium is seven-coordinate owing to alkoxide bridging and bidentate behavior of the acetate group. In contrast, the structure of **4** (Z = $OSiPh_3$) determined by X-ray means is monomeric owing to the bulk of the apical siloxy group. Variable-temperature ^1H and ^{13}C NMR studies allow the categorization of the titanatranes studied into three classes: those displaying monomeric behavior in solution at room temperature (Z = O-*i*-Pr, (**1**), Cp (**3**), $OSiPh_3$ (**4**), and O-*t*-Bu (**5**)), those behaving as dimers undergoing a fluxional gearing motion at room temperature but becoming monomeric upon warming (Z = Cl (**2**), **6**, **7**), and titanatrane **8**, which behaves as a rigid dimer at room temperature. Crystallographic parameters for **4** are space group $R\bar{3}$, a = 9.5689 (5) Å, b = 45.411 (4) Å, Z = 6, while for **7** they are space group $P2_1/n$, a = 15.563 (3) Å, b = 6.872 (1) Å, c = 19.743 (4) Å, β = 106.65 (1)°, Z = 2.

Introduction

The chemistry of atrane structures has been most intensely studied for silicon,[1] tin,[2] and phosphorus.[3] At the time we began our studies of titanatranes, only the molecular structure of **1**,



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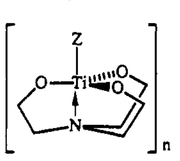

	Z		Z
2	Cl	6	OPh
3	Cp	7	O(O)CMe
4	$OSiPh_3$	8	NMe_2
5	O-*t*-Bu		

determined by X-ray means, had been reported and a synthesis for **4** had been described.[5] A very recent report on the synthesis and interconversion of **2** and **3**[6] prompts us to describe here our routes to **5**–**8** and additionally our independent synthesis of **2**–**4**. Also reported are solution and solid-state X-ray structural evidence for the monomeric titanatrane **4** and the unexpected *seven*-coordinate dimeric titanatrane dimer **7**.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified argon at room temperature by using standard inert-atmosphere and Schlenk techniques[7] unless otherwise stated. Tetrahydrofuran (THF), toluene, benzene, and Et_2O were distilled from Na/benzophenone under N_2. Triethanolamine (TEA) was distilled under vacuum and stored over 4-Å type molecular sieves. Hexane and chloroform were distilled from phosphorus(V) oxide under argon. ^1H NMR and ^{13}C NMR spectra were recorded on a Nicolet NT-300 300-MHz spectrometer using the protio impurity of the solvent as internal reference. Variable-temperature NMR spectra were obtained on a Bruker WM-200 200-MHz or a Varian VXR-300 300-MHz instrument. FT-IR spectra were recorded on an IBM-IR98 spectrometer as solids in KBr pellets or Nujol mulls. Mass spectra were obtained on a Finnigan 4000 instrument or a Kratos MS-50 spectrometer.

The starting materials $Ti(O\text{-}t\text{-}Bu)_4$,[8] $Ti(NMe_2)_4$,[9] and $CpTi(OMe)_3$[10] were prepared by using methods published in the literature.

(2-Propanolato)titanatrane (1). The synthesis of this compound was analogous to that of **5** (see below): 2.10 g, 83% yield, mp dec; ^1H NMR ($CDCl_3$) δ 1.27 (d, 6 H), 3.13 (t, 6 H), 4.40 (t, 6 H), 4.61 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.82 (CH_3), 56.12 (CH_2N), 70.36 (CH_2O), 77.12 (CHO).

Chlorotitanatrane (2).[6] A solution of 1.90 g (10 mmol) of $TiCl_4$ in 30 mL of $CHCl_3$ was cooled in an ice bath and saturated with dry NH_3 gas. After 30 min, 1.49 g (10 mmol) of TEA in 10 mL of $CHCl_3$ was added to the yellow suspension and the mixture was stirred overnight. The suspension was filtered, and the filtrate was concentrated in vacuo to give 1.67 g (72%) of off-white solid crude product. This was recrystallized from CH_2Cl_2 to give white needles: mp dec; ^1H NMR ($CDCl_3$) δ 3.31 (br s, $\nu_{1/2}$ = 30 Hz, 6 H), 4.53 (br s, $\nu_{1/2}$ = 30 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 59.47 (CH_2N), 72.47 (CH_2O); MS (EI) *m/e* 229, 231 (M^+, 5.3% and 2.3%), 199 ($M^+ - CH_2O$, 100%), 169 ($M^+ - 2CH_2O$, 38.6%); IR (KBr, cm^{-1}) 1259 m, 1097 s, 1066 vs, 929 m, 904 m, 744 m, 610 m, 534 m.

Cyclopentadienyltitanatrane (3).[6] A solution of 0.75 g (5 mmol) of TEA in 10 mL of THF was added dropwise to 1.03 g (5 mmol) of $CpTi(OCH_3)_3$ dissolved in 20 mL of THF. The white precipitate was filtered out and recrystallized from benzene: 0.97 g, 75% yield; mp dec; ^1H NMR ($CDCl_3$) δ 2.99 (t, 6 H), 4.32 (t, 6 H), 6.33 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 55.65 (CH_2N), 70.94 (CH_2O), 116.64 (Cp); HRMS (EI) for M^+, $C_{11}H_{17}NO_3Ti$: found, *m/e* 259.06833; calc, *m/e* 259.06879.

(Triphenylsilanolato)titanatrane (4). This synthesis was analogous to that of **6** (see below). The crude product was crystallized from toluene: 3.69 g, 78% yield; mp 271–272 °C (lit[6] mp 268–270 °C); ^1H NMR ($CDCl_3$) δ 3.16 (t, 6 H), 4.48 (t, 6 H), 7.28–7.75 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 56.91 (CH_2N), 71.54 (CH_2O), 127.47, 129.19, 135.19, 135.32; MS (EI) *m/e* 469 (M^+, 0.01%), 468 ($M^+ - H$, 0.06%), 439 ($M^+ - CH_2O$, 6.8%), 409 ($M^+ - C_6H_5$, 100%); HRMS (EI) for $M^+ - CH_2O$, $C_{23}H_{25}NO_3SiTi$: found, *m/e* 439.10856; calcd, *m/e* 439.10832; IR (KBr, cm^{-1}) 1259 m, 1116 s, 1103 s, 1080 m, 1056 vs, 1031 s, 1008 s, 991 s, 925 s, 904 s, 609 m, 513 m.

(2-Methyl-2-propanolato)titanatrane (5). A solution of 3.46 g (10.2 mmol) $Ti(O\text{-}t\text{-}Bu)_4$ in 15 mL of THF was added dropwise to a solution of 1.49 g (10.0 mmol) of TEA in 20 mL of THF and stirred for 30 min. The volatiles were removed in vacuo, and the crude product was recrystallized from benzene: 2.40 g, 90% yield of colorless crystals; mp 156–158 °C; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 3.15 (t, 6 H), 4.42 (t, 6 H); ^{13}C NMR ($CDCl_3$) δ 31.47 (CH_3), 55.81 (CH_2N), 70.16 (CO); MS (EI) *m/e* 252 ($M^+ - CH_3$, 100%), 237 ($M^+ - C_2H_6$, 64%), 207 ($M^+ - C_3H_8O$, 23%), 194 ($M^+ - C_4H_9O$, 65%); IR (KBr, cm^{-1}) 1261 w, 1230 w, 1193 w, 1103 s, 1064 vs, 1010 s, 923 w, 900 m, 792 w, 590 m (ν(Ti–OR)); HRMS (EI) for $M^+ - CH_3$, $C_9H_{18}NO_4Ti$: found, *m/e* 252.07082; calcd, *m/e* 252.07153.

(Phenolato)titanatrane (6). A solution of 3.40 g (10.0 mmol) $Ti(O\text{-}t\text{-}Bu)_4$ in 10 mL of THF was added dropwise to 0.94 g (10.0 mmol) of phenol in 15 mL of THF and stirred for 1 h. TEA (1.49 g, 10.0 mmol) in 10 mL of THF was added dropwise to the yellow solution, and stirring was continued for an additional 1 h. The volatiles were removed in vacuo, and the yellow crude product was dried under vacuum for 17 h at 60 °C: 2.45 g, 85% yield; mp 95–105 °C; ^1H NMR ($CDCl_3$) δ 3.30 (br s, $\nu_{1/2}$ = 30 Hz, 6 H), 4.58 (br s, $\nu_{1/2}$ = 30 Hz, 6 H), 6.7–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 58.65 (CH_2N), 72.14 (CH_2O), 118.43, 119.63, 126.6; HRMS (EI) for M^+, $C_{12}H_{17}NO_4Ti$: found, *m/e* 287.06400; calcd, *m/e* 287.6370); IR (Nujol, cm^{-1}) 1587 s, 1481 s, 1269 s, 1097 s, 1072

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[1] See for example: (a) Voronkov, M. G.; Dyakov, V. M.; Kirpichenkov, S. V. *J. Organomet. Chem.* **1982**, *233*, 1. (b) de Ruiter, B.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 1065. (c) Woning, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 944.

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Table I. Crystallographic Data for **4** and **7**

	4	**7**
formula	$C_{24}H_{27}NO_4SiTi$	$C_{16}H_{30}N_2O_{10}Ti_2\cdot 4CHCl_3$
fw	469.47	983.74
space group	$R\bar{3}$	$P2_1/n$
a, Å	9.5689 (5)	15.563 (3)
b, Å	45.411 (4)	6.872 (1)
c, Å		19.743 (4)
β, deg		106.65 (1)
V, Å^3	3600.9 (3)	2022 (1)
Z	6	2
d_{calc}, g/cm^3	1.299	1.615
cryst size, mm	0.45 × 0.46 × 0.42	0.2 × 0.3 × 0.6
μ(Mo Kα), cm^{-1}	4.277	12.356
data colln instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (monochromated in incident beam) (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
orientation reflcns: no.; range (2θ), deg	25; 20.4–32.2	25; 17.8 < 2θ < 34.9
temp, °C	−70 (1)	−50 (1)
scan method	θ–2θ	θ–2θ
data colln range (2θ), deg	4.0–50.0	4.0–45.0
no. of data collcd	1411	5799
no. of unique data: tot. with $F_o^2 > 4\sigma(F_o^2)$	1186	2905
no. of params refined	95	208
max, min transm factors (ψ scans)	0.9991, 0.9491	0.994, 0.828
R^a	0.033	0.063
R_w^b	0.055	0.086
quality-of-fit indicator^c	1.27	2.23
largest shift/esd, final cycle	0.01	0.01
largest peak, e/Å^3	0.25 (4)	0.63 (9)

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

vs, 881 m, 757 m, 648 m, 558 m, 512 m.

(Acetato)titanatrane (7). This synthesis was analogous to that of **6**. The crude product was recrystallized from chloroform: 2.08 g, 82% yield; mp 185–186 °C; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3 H), 3.30 (br s, $\nu_{1/2}$ = 165 Hz, 6 H), 4.65 (br s, $\nu_{1/2}$ = 45 Hz, 6 H); ^{1}H NMR ($CDCl_3$, 60 °C) δ 2.05 (s, 3 H), 3.47 (t, 6 H), 4.73 (t, 6 H); ^{1}H NMR (CD_2Cl_2, −60 °C) δ 2.01 (s, 3 H), 3.14–3.22 (m, 4 H), 3.94 (virt dt, 2 H), 4.41 (virt dd, 2 H), 4.60–4.76 (virt t + dt, 4 H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 23.29 (CH_3), 62.32 (CH_2N), 74.20 (CH_2O), 186.31 (C═O); MS (EI) *m/e* 253 (M^+, 0.2%), 238 ($M^+ - CH_3$, 10.7%), 223 ($M^+ - CH_2O$, 100%), 193 ($M^+ - CH_3CO_2H$, 58.9%); IR (KBr, cm^{-1}) 1577 s, 1446 s, 1085 s, 1070 vs, 1035 s, 1028 s, 921 m, 902 s, 688 m, 651 m, 622 m, 597 m.

(Dimethylamino)titanatrane (8). A solution of 0.64 g (4.3 mmol) of TEA in 20 mL of THF is added in one portion to a stirred solution of 1.00 g (4.5 mmol) of $Ti(NMe_2)_4$ dissolved in 20 mL of THF and stirred overnight. A yellow microcrystalline solid separated from the solution. The volatiles were removed in vacuo, and the crude product was recrystallized from THF in 84% yield: mp dec; ^{1}H NMR (C_6D_6) δ 2.23–2.37 (m, 4 H), 2.69 (virt q, 2 H), 3.74 (s, 6 H), 4.24 (t, 2 H), 4.33–4.52 (m, 4 H); ^{13}C NMR (C_6D_6) δ 50.97 (CH_3N), 57.49 (CH_2N), 62.95 (2 × CH_2N), 69.37 (CH_2O), 71.48 (2 × CH_2O); ^{13}C NMR (C_6D_6, 60 °C) δ 50.27 (CH_3N), 61.69 (CH_2N), 70.96 (CH_2O). Anal. Calcd for $C_8H_{18}N_2O_3Ti$: C, 40.38; H, 7.61; N, 11.38. Found: C, 40.35; H, 7.62; N, 11.76.

Crystal Structure Analysis of 4. A colorless crystal was mounted on the end of a glass fiber, moved to the diffractometer, and cooled to −70 ± 1 °C. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table I. Lorentz and polarization corrections were applied as well as absorption corrections based on ψ scans. Data reduction was performed using the CAD4-SDP programs.[11] The choice of the centric space group *R*3 was indicated by intensity statistics and verified by the successful refinement of the structure. The positions of all 13 unique atoms were taken from a direct-methods *E* map.[12] The molecule resides on a crystallographic 3-fold axis so that the Si–O–Ti–N linkage is perfectly linear. Hydrogen atoms were added in idealized positions with a C–H bond length of 0.95 Å and were used for structure factor calculations only. In the final refinement cycles, all non-hydrogen atoms were refined with anisotropic temperature factors and an extinction coefficient was refined to a value of 1 (1) × 10^{-7} (in absolute units). Neutral-atom scattering factors and anomalous scattering corrections were taken from the usual source.[13] Positional parameters are given in Table II, and an ORTEP drawing is shown in Figure 1.

Table II. Positional Parameters and Their Estimated Standard Deviations for **4**

atom	*x*	*y*	*z*	*B*,^{a} Å^2
Ti	0.000	0.000	0.15191 (1)	2.627 (7)
Si	0.000	0.000	0.07611 (2)	2.64 (1)
O(1)	0.000	0.000	0.11153 (5)	3.55 (3)
O(2)	0.0413 (1)	0.2048 (1)	0.16012 (3)	3.41 (3)
N	0.000	0.000	0.20176 (6)	3.17 (4)
C(1)	0.0686 (2)	0.2720 (2)	0.18892 (4)	3.85 (4)
C(2)	−0.0243 (5)	0.1355 (2)	0.21053 (4)	3.82 (4)
C(3)	−0.0013 (2)	0.1839 (2)	0.06285 (4)	3.23 (4)
C(4)	0.0824 (2)	0.3274 (2)	0.07903 (5)	4.42 (5)
C(5)	0.0846 (3)	0.4655 (3)	0.07003 (7)	5.91 (6)
C(6)	0.0061 (3)	0.4657 (3)	0.04545 (7)	7.20 (7)
C(7)	−0.0797 (3)	0.3268 (3)	0.02882 (6)	7.14 (7)
C(8)	−0.823 (3)	0.1839 (3)	0.03749 (5)	4.94 (5)

^{a} *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

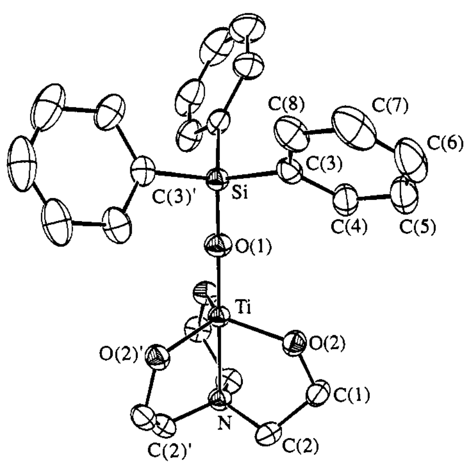

Figure 1. ORTEP drawing of **4**, with ellipsoids drawn at the 50% probability level.

Scheme I

$$TiZ_4 \xrightarrow{\text{TEA}} \mathbf{1}\ (Z = i\text{-PrO}),\ \mathbf{5}\ (Z = t\text{-BuO}),\ \mathbf{8}\ (Z = NMe_2) \qquad (1)$$

$$T(O\text{-}t\text{-Bu})_4 \xrightarrow{\substack{\text{1. HZ}\\ \text{2. TEA}}} \mathbf{4}\ (Z = OSiPh_3),\ \mathbf{6}\ (Z = OPh),\ \mathbf{7}\ (Z = O_2CMe) \qquad (2)$$

$$TiCl_4 \xrightarrow{\substack{\text{1. } NH_3\\ \text{2. TEA}}} \mathbf{2}\ (Z = Cl) \qquad (3)$$

$$CpTi(OMe)_3 \xrightarrow{\text{TEA}} \mathbf{3}\ (Z = Cp) \qquad (4)$$

Crystal Structure Analysis of 7. A colorless crystal was mounted on the end of a glass fiber, moved to the diffractometer, and cooled to −50 ± 1 °C. The cell constants were determined from a list of reflections found by an automated search routine, and the Laue symmetry of the cell was confirmed by photography. Pertinent data collection and reduction information is given in Table I. Lorentz and polarization corrections were applied. The intensity standards indicated a total decay of 6.8%, so an anisotropic decay correction was applied. An absorption

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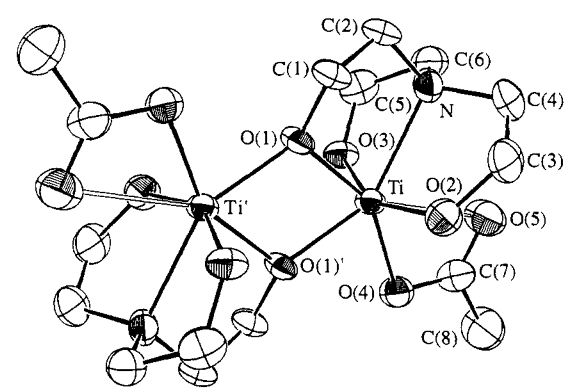


Figure 2. ORTEP drawing of 7, with ellipsoids drawn at the 50% probability level.

Table III. Positional Parameters and Their Estimated Standard Deviations for **7**

atom	*x*	*y*	*z*	B,[a] Å^2
Ti	0.07846 (7)	0.0288 (2)	0.45999 (5)	2.17 (3)
O(1)	−0.0479 (3)	0.1095 (9)	0.4617 (2)	2.4 (1)
O(2)	0.0336 (3)	−0.120 (1)	0.3809 (2)	3.3 (1)
O(3)	0.1317 (3)	0.2522 (9)	0.5021 (2)	2.8 (1)
O(4)	0.1942 (3)	−0.1258 (9)	0.4980 (2)	3.1 (1)
O(5)	0.2162 (3)	0.036 (1)	0.4101 (3)	4.5 (2)
N	0.0388 (3)	0.257 (1)	0.3720 (2)	2.9 (2)
C(1)	−0.1060 (4)	0.180 (1)	0.3964 (3)	2.8 (2)
C(2)	−0.0512 (4)	0.329 (1)	0.3692 (3)	3.4 (2)
C(3)	0.0048 (5)	−0.051 (2)	0.3091 (3)	4.5 (2)
C(4)	0.0397 (5)	0.148 (2)	0.3059 (3)	4.0 (2)
C(5)	0.1276 (4)	0.436 (2)	0.4706 (4)	3.8 (2)
C(6)	0.1064 (4)	0.412 (2)	0.3909 (4)	3.8 (2)
C(7)	0.2433 (4)	−0.079 (2)	0.4586 (4)	3.5 (2)
C(8)	0.3345 (5)	−1.69 (2)	0.4765 (5)	6.4 (3)
C(9)	0.7949 (5)	0.272 (2)	0.1329 (4)	5.9 (3)
Cl(1)	0.8438 (1)	0.4997 (5)	0.1678 (1)	6.14 (8)
Cl(2)	0.7532 (2)	0.1642 (6)	0.1966 (1)	8.9 (1)
Cl(3)	0.8723 (2)	0.1337 (8)	0.1101 (2)	12.1 (1)
C(10)	0.1407 (6)	0.743 (3)	0.1475 (6)	11.0 (4)
Cl(4)	0.0745 (2)	0.5553 (8)	0.1733 (2)	10.5 (1)
Cl(5)	0.0694 (4)	0.863 (1)	0.0825 (4)	19.1 (3)
Cl(6)	0.1945 (3)	0.8746 (9)	0.2180 (3)	21.5 (2)

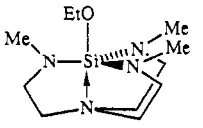
[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^{2*}B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

correction based on a series of ψ scans was also applied. The space group was unambiguously indicated by the systematic absences. The positions of the Ti atom and the Cl atoms of the solvent molecules were taken from a direct-methods E map.[12] The remainder of the non-hydrogen atoms were located in a subsequent difference Fourier map. In the final stages of refinement, all non-hydrogen atoms were given anisotropic temperature factors. Isotropic temperature factors for the hydrogen atoms were fixed at 1.3 times the isotropic equivalent B value for the corresponding carbon atoms. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SPD programs.[11] Neutral-atom scattering factors and anomalous scattering corrections were taken from the usual source.[13] Positional parameters are given in Table III, and an ORTEP drawing is shown in Figure 2.

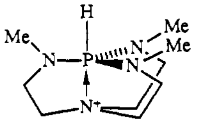
Results and Discussion

Syntheses. Titanatranes **1**–**8** were obtained in high yields as crystalline solids (except for **6**, which was an amorphous yellow solid) by the routes summarized in reactions 1–4 of Scheme I. Unlike their silicon analogues, compounds **1**–**8** are not very volatile, and they decompose upon attempted sublimation under vacuum. They do, however, display parent ions for the monomeric cage units in their mass spectra. NMR tube experiments indicate that more acidic hydroxyl groups displace the alkoxo groups in **1** and **5**, forming less acidic hydroxyl compounds. Moreover, the Cp group is displaced by all the hydroxyl compounds tested (i.e., *i*-PrOH, *t*-BuOH, PhOH, Ph_3SiOH, and $MeCO_2H$) but not by amines. Compound **2** converts to **1** or **5** in the presence of the corresponding alcohol and an amine base. The interconversion of **2** and **3** has been described previously.[6]

Solid-State Structures of 4 and 7. As shown in Figure 1, **4** is monomeric in the solid state, presumably because of the bulky nature of the $OSiPh_3$ group. The geometry around the titanium is nearly trigonal bipyramidal with the metal atom about 37 pm above the plane of the equatorial oxygens. The linear Si–O–Ti–N axis contains a transannular Ti–N bond having a length of 226.4 pm, which compares favorably with that in the dimeric structure **1** (233.3 pm[4]). These transannular Ti–N distances are considerably longer than their counterparts in four-coordinate titanium(VI) amides such as $(\eta^1\text{-Cp})_2Ti[\overline{N(CH)_3CH}]_2$ (average 208.5(5) pm[14]) and $[\eta^5\text{-}C_5H_4Ti(NEt_2)_3]_2Fe$ (average 188 pm[15]). The lengthening of the transannular bond from the tertiary amine to titanium in **1**, **4**, and **7** over the amide nitrogen–titanium bonds in the aforementioned four-coordinate Ti(IV) compounds by about 15% is comparable to those observed in **9** (22%[16]) and **10** (19%[17])



9



10

over the respective E–amide bond lengths in these compounds. All the Ti–O distances in **4** (183.4 pm) are similar to those found for the terminal alkoxy group(s), in **1**,[4] $[Ti(OMe)_4]_4$,[18] $[LiTi(O\text{-}i\text{-}Pr)_5]_2$,[19] and $Ti(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OBu)_2(OBu)_6(OAc)_6$.[20]

As shown in Figure 2, **7** is a dimer in the solid state (which crystallizes with four molecules of chloroform solvent). A striking feature of the structure is the seven-coordinate nature of the titanium atoms, which contrasts with the six-coordinate octahedral geometry found in **1**,[4] $Na_4[Ti_2O_5(C_6H_6O_6)_2\cdot 11H_2O$,[21] and in other titanium alkoxides.[18,22,23] The geometry around each titanium in **7** can be viewed as a distorted trigonal prism of oxygen atoms with a nitrogen near a rectangular face. To accommodate the chelating carbonyl oxygen of the acetato group, the O(2)–Ti–O(3) angle opens to 150.4 (2)° compared with the 115.98 (3)° found in **4**. The O(5)–Ti distance (260.3 (4) pm) is considerably larger than the O(4)–Ti length (204.0 (4) pm), suggesting that O(5) of the acetato group is more carbonyl-like than O(4). This is also reflected in the shorter C(7)–O(5) distance (121.9 (8) pm) compared with C(7)–O(4) (127.9 (6) pm). These distances are also comparable to those found in the unidentate acetato group (120 and 133 pm).[24] The separation (131 cm^{-1}) in the carboxyl stretches (1577, 1446 cm^{-1}) in the KBr IR spectrum of **7** is also in agreement with bidentate acetato coordination.[25] The weaker interaction of O(5) with the metal can be ascribed to repulsions from O(2) and O(3) encountered in spreading the ethanolato bridges apart. However, the opening of the O(2)–Ti–O(3) angle is not registered in the C(4)–N–C(6) angle, since all three C–N–C angles are substantially the same. The metal-metal distance in **4** (329.0 (2) pm) is shorter than in **1** (335.6 (1) pm) but not indicative of any substantial Ti–Ti interaction. The Ti–N distance

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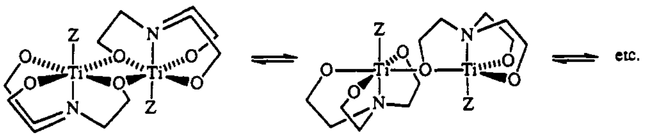
Scheme II



in 7 (229.0 (5) pm) is within experimental error of that in 4 (226.4 (3) pm)).

NMR Spectra. Titanatranes **1**-**8** can be divided into three categories on the basis of their NMR spectra in $CDCl_3$ as a function of temperature. In the first category are **1**, **3**, **4**, and **5**, whose ^1H and ^{13}C NMR spectra are largely temperature-independent. Because of the bulky nature of the apical substituents, these compounds display spectra consistent with monomeric behavior. In the case of **1**, some broadening of the ^1H NMR signals can be observed at -60 °C, owing to the relatively decreased bulk of the *i*-Pr group, which allows this compound to form a dimer in the solid state.

Titanatranes **2**, **6**, and **7** constitute a class for which the ^1H and ^{13}C NMR spectra are broadened at room temperature, presumably owing to an exchange process which is slow on the NMR time scale. Because dilution of solutions of these dimers does not affect the breadth of the ^1H NMR peaks of these compounds, the exchange process can be envisioned as being dominated by an intramolecular "gearing" fluxional motion around their Z-Ti-N axes (depicted in Scheme II) rather than by a dissociation into monomers. This gearing motion requires the breakage of only one bridge bond at a time with the subsequent formation of a new one as opposite rotations about the Z-Ti-N axes occur. At 60 °C the ^1H NMR resonances become sharp for **2**, **6**, and **7**, and a single time-averaged spectrum is observed wherein the three CH_2CH_2O groups are equivalent. At -60 °C the ^1H NMR spectra are still broad for **2** and **6**, whereas for **7** the exchange process is essentially frozen out and two types of CH_2CH_2O groups can be distinguished in a 2:1 ratio. The coalescence temperature for this process in $CDCl_3$ is +10 °C. Presumably because of the bidentate nature of the acetato group in **7**, the gearing fluxionality for this dimer is less facile than for **2** and **6**. These dimers are robust to adduct formation by strong donors. Thus, addition of pyridine, DMSO, acetone, and acetonitrile failed to reveal NMR evidence for interaction with these compounds.

In the case of **8**, the ^1H and ^{13}C NMR spectra at room temperature display sharp resonances for two types of CH_2CH_2O groups in a 2:1 ratio consistent with the presence of a stable dimer. Upon heating, the ^{13}C NMR resonances broaden until at 60 °C only one type of CH_2CH_2O group is observed. The relative robustness of dimeric **8** compared with dimers **2**, **6**, and **7** may be ascribed to an electron donation effect of the Me_2N group which enhances oxygen bridging as in **1**. A final conclusion on this point depends on the growth of crystals of **8** suitable for X-ray diffraction experiments.

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Registry No. 1, 87654-61-3; 2, 136736-74-8; 3, 136736-75-9; 4, 6026-51-3; 5, 136736-76-0; 6, 15364-28-0; 7, 136736-78-2; 8, 136736-79-3; $CpTi(OCH_3)_3$, 12145-64-1.

Supplementary Material Available: Tables of bond distances, bond angles, least-squares planes, positional and thermal parameters for calculated hydrogen atoms, and general displacement parameter expressions (12 pages); tables of structure factors (15 pages). Ordering information is given on any current masthead page.

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Preparation of Unsymmetrically B-Substituted Borazines and Characterization of Tris(4,6-diethylborazin-2-yl)amine

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Symmetrically substituted *B,B′,B″*-triorganylborazines, $(RBNR')_3$, react with an equimolar quantity of boron trihalide, BX_3 (X = Cl, Br), to form *B*-monohaloborazines, $XR_2B_2N_3R_3$, as well as RBX_2, and with 2 molar equiv of BX_3 to form the *B,B′*-dihaloborazines, $X_2RB_3N_3R'_3$. The compounds are obtained in good yield and purity, and are easily converted to other unsymmetrically B-substituted borazines. The borazines $X(CH_3)_2B_3N_3(CH_3)_3$ (X = SCH_3, NH_2, C_4H_9, $N[Si(CH_3)_2]$), $X(C_2H_5)_2B_3N_3H_3$ (X = Br, SCH_3), $Cl(C_2H_5)_2B_3N_3(CH_3)_3$, $X_2(C_2H_5)_2B_3N_3H_3$ (X = Br, SCH_3), $Cl(C_6H_5)_2B_3N_3H_3$, and $Cl_2(C_2H_5)B_3N_3(CH_3)_3$ have been prepared and characterized. The compound $(H_2N)(C_2H_5)_2B_3N_3H_3$ could not be obtained in the pure state; instead, it slowly condenses (even at room temperature) with the formation of the bis(borazin-2-yl)amine $HN[(C_2H_5)_2B_3N_3H_3]_2$ and the tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_3$. The borazine $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ condenses at temperatures from 250 to 270 °C to give $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$. Reaction of this bis(borazin-2-yl)amine with LiC_4H_9 yields $(C_4H_9)(CH_3)_2B_3N_3(CH_3)_3$ and $(NHLi)(CH_3)_2B_3N_3(CH_3)_3$; the latter then reacts with $Cl(CH_3)_2B_3N_3(CH_3)_3$ to regenerate $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$. The unsymmetrically N-substituted borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been isolated and characterized.

Introduction

Borazine is the foremost example of an inorganic compound that can be closely compared to an organic species, i.e., benzene. Hence, studies on this six-membered B_3N_3 heterocyclic system have been popular and literally hundreds of borazine derivatives are known. However, most of them are symmetrically substituted species of the type $(RBNR')_3$. Relatively few unsymmetrically substituted derivatives have been described and their chemistry has been investigated only sparingly.[1]

Within the context of preparative studies on discrete polycyclic boron-nitrogen systems as potential precursors for macromolecular materials, the synthesis of the tris(borazin-2-yl)amine framework seemed to be an interesting point of origin. Detailed studies on such species require convenient access to unsymmetrically B-substituted borazines of the types $XR_2B_3N_3R'_3$ and $X_2RB_3N_3R'_3$ (and where X is a reactive site) in high purity. The present report describes the preparation and characterization of various such unsymmetrically B-substituted borazines as well as attempts to synthesize the tris(borazin-2-yl)amine skeleton.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 or XL-200 (^{11}B) or GEMINI-200 (^1H,

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