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Titanatranes and Azatitanatranes: Nucleophilic Substitution Reactions on the Axial Position

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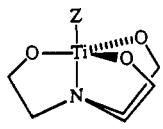
The titanatrane $Me_2NTi(OCH_2CH_2)_3N$ (**8**) is shown to be labile to substitution of the axial NMe_2 group by a variety of OR groups in reactions with the corresponding ROH reagent to give $ZTi(OCH_2CH_2)_3N$ in better than 90% yield where Z is O-*i*-Pr (**1**), $OSiPh_3$ (**4**), O-*t*-Bu (**5**), OPh (**6**), and $OCMe_2Et$ (**9**). RSH compounds also cleanly react with **8** to give analogous products, in better than 85% in most cases, wherein Z is SEt (**10**), S-*i*-Pr (**11**), $SCMe_2Et$ (**12**), SPh (**13**), and *S*-allyl (**14**). The lability of **8** to nucleophilic substitution is related in part to its unique oxygen-bridged centrosymmetric dimeric structure which in contrast to **1** features each monodentate axial substituent trans to an oxygen rather than to the tertiary nitrogen. Crystallographic parameters for **8** are space group $P2_1/c$, a = 11.154 (5) Å, b = 10.942 (2) Å, c = 9.708 (5) Å, α = 90.0°, β = 115.4 (2)°, γ = 90.0°, and Z = 2. In contrast, the new azatitanatrane $Me_2NTi(MeNCH_2CH_2)_3N$ (**15**) does not display susceptibility to nucleophilic displacement of its axial Me_2N group, decomposing instead. The compound *t*-$BuOTi(MeNCH_2CH_2)_3N$ was synthesized in 54% yield, however, by reacting $Ti(NMe_2)_4$ with 1 equiv of *t*-BuOH followed by 1 equiv of $(MeNHCH_2CH_2)_3N$.

Introduction

Only three reports of titanatranes (i.e., **1**–**8**) have thus far appeared.[1-3] Recently, these interesting polycyclic metal alkoxide systems were discovered to fall into three classes according to their



Z	Z	Z
1 O-*i*-Pr[1]	6 OPh[4]	11 S-*i*-Pr
2 Cl[2,4]	7 O(O)CMe[4]	12 $SCMe_2Et$
3 Cp[2,4]	8 NMe_2[4]	13 SPh
4 $OSiPh_3$[3,4]	9 $OCMe_2Et$	14 S-allyl
5 O-*t*-Bu[4]	10 SEt	

variable-temperature solution NMR characteristics. Thus **1**, **3**, **4**, and **5** displayed monomeric behavior at room temperature, **2**, **6**, and **7** featured fluxional dimeric behavior at room temperature (but becoming monomeric upon warming), and **8** exhibited rigid dimeric behavior at room temperature.[4] Prior to our earlier report of the molecular structures of **4** and **7** determined by X-ray means (see configurations in Chart I),[4] the only solid-state structure determined for a titanatrane was that shown below for **1**.[1] In our previous paper,[4] we showed from X-ray diffraction studies that **4** and **7** contain five-coordinate and seven-coordinate metal atoms, respectively, as depicted in Chart I. Here we report that the solid-state structure of **8** displays yet a different coordination geometry in the solid state. Moreover, **8** undergoes facile substitution of its dimethylamino group by ROH to give **1**, **4**, **5**, **6**, and **9** and by RSH to give **10**–**14** in good yields.

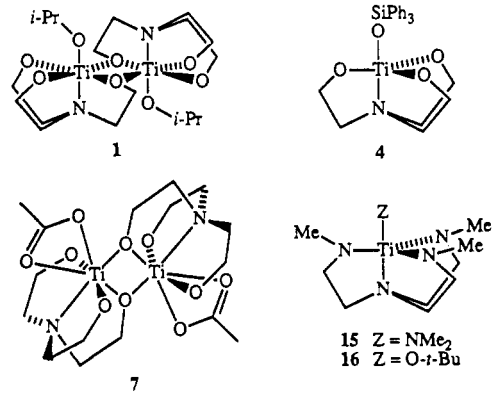
Azatitanatranes (i.e., titanatranes with their equatorial oxygens replaced by NR groups) do not seem to have been reported. Here we describe our synthesis of **15** and **16**, which constitute the first members of a new class of polycyclic titanium amides.

Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were recorded on a Nicolet NT-300 300 MHz spectrometer using the proton impurity of the solvent as internal reference. Variable-temperature NMR spectra were run on a Bruker WM-200 200-MHz or a Varian VXR-300 300-MHz instrument. Mass spectra were obtained on a Finnigan 4000 instrument or a Kratos MS-50 spectrometer. FT-IR spectra were recorded on an IBM-IR98 spectrophotometer as a solid in KBr pellets or as Nujol mulls. Melting points were determined by a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN.

All reactions were carried out under an atmosphere of prepurified argon at room temperature by using standard inert-atmosphere and Schlenk techniques.[5] Tetrahydrofuran (THF), toluene, benzene, Et_2O, and pentane were distilled from Na/benzophenone under nitrogen. Dichloromethane was distilled from calcium hydride under argon. Triethanolamine (TEA) was distilled under vacuum and stored over type 4A molecular sieves. The starting materials $Ti(NMe_2)_4$[6] and $(MeHNCH_2CH_2)_3N$[7] were prepared using published methods.

Chart I



Preparation of $Me_2EtCOTi(OCH_2CH_2)_3N$ (9). Compound **8** (0.52 g, 2.2 mmol) was reacted with *tert*-amyl alcohol (0.23 mL, 0.19 g, 2.2 mmol) in 20 mL of dry methylene chloride. After being stirred for 10 min at room temperature, the color changed from yellow to colorless, indicating the end of the reaction. The contents of the reaction flask were layered with pentane and cooled at −25 °C. Small crystals grew overnight in 96% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3CH_2), 1.29 (s, 6 H, $(CH_3)_2$), 1.59 (q, 2 H, $^3J_{HH}$ = 7.5 Hz, CH_3CH_2), 3.11 (t, 6 H, $^3J_{HH}$ = 5.4 Hz, NCH_2), 4.39 (t, 6 H, $^3J_{HH}$ = 5.4 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 9.10 (CH_2CH_3), 28.94 ($(CH_2)_2$), 36.99 (CH_2CH_3), 55.79 (CH_2N), 70.15 (CH_2O), 84.61 (CMe_2Et); IR (Nujol, cm^{-1}) 2979, 2845, 2682, 1463, 1376, 1357, 1026, 815, 452; MS *m/e* (relative intensity) 266 (25, M^+ − Me), 252 (100, M^+ − Et), 251 (54, M^+ − 2Me), 210 (1, M^+ − CMe_2Et), 194 (82, M^+ − $OCMe_2Et$). Anal. Calcd for $C_{11}H_{23}NO_4Ti$: C, 46.99; H, 8.24; N, 4.98. Found: C, 46.83; H, 7.96, N, 5.07.

Preparation of $ROTi(OCH_2CH_2)_3N$ (R = O-*i*-Pr) (1),[1] $OSiPh_3$ (4),[4] O-*t*-Bu (5),[4] OPh (6)[4]. Stoichiometric amounts of the appropriate alcohol or silanol were added to **8** dissolved in methylene chloride. After being stirred for 10–30 min, the reaction mixture was layered with pentane and cooled to −25 °C. Colorless crystals were separated and characterized by ^1H and ^{13}C NMR spectroscopy. The yields in all cases were better than 90%.

Preparation of $[EtSTi(OCH_2CH_2)_3N]_2$ (10). To a solution of (dimethylamino)titanatrane (0.48 g, 2.0 mmol) in 20 mL of dry methylene

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(7) (a) Lensink, C.; Xi, S. K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *111*, 3478. (b) Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214.

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chloride was added 0.15 mL (2.0 mmol) of ethanethiol. The reaction mixture was stirred for 4 h at room temperature and then layered with pentane and placed at 0 °C. Yellow microcrystals appeared overnight in 87% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 6 H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 2.89 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, CH_2N), 3.08–3.18 (m, 4 H, CH_2N), 3.38 (q, 4 H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 3.42–3.52 (m, 4H, CH_2N), 4.53 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, CH_2O), 4.65–4.74 (m, 4 H, CH_2O, 4.87–4.96 (m, 4 H, H_2O; ^{13}C NMR ($CDCl_3$) δ 19.72 (CH_2CH_3), 29.95 (CH_2CH_3), 57.21 (NCH_2), 60.73 (2 C, NCH_2), 72.83 (2 C, OCH_2), 75.84 (OCH_2); IR (Nujol, cm^{-1}) 2955, 2924, 2853, 1462, 1377, 1341, 1057, 901, 722, 567; MS *m/e* (relative intensity) 255 (5, M^+), 226 (1, M^+ – Et), 194 (17, M^+ – SEt); mp 92 °C dec.

Preparation of [*i*-PrSTi(OCH$_2$CH$_2$)$_3$N]$_2$ (11). The procedure is the same as for compound **10**: yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (d, 12 H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$), 2.90 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, NCH_2), 3.09–3.16 (m, 4 H, NCH_2) 3.43–3.52 (m, 4 H, NCH_2), 4.08 (h, 2 H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$), 4.56 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, OCH_2), 4.72–4.80 (m, 4 H, OCH_2), 4.84–4.91 (m, 4 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 28.25 ($CH(CH_3)_2$), 40.09 ($CH(CH_3)_2$), 57.40 (NCH_2), 61.85 (2 C, NCH_2), 73.50 (2 C, OCH_2), 76.29 (OCH_2); IR (Nujol, cm^{-1}) 2951, 2923, 2852, 1457, 1375, 1097, 903, 639, 540, MS *m/e* (relative intensity) 269 (35, M^+), 254 (2, M^+ – Me), 239 (13, M^+ – 2Me), 226 (1, M^+ – $CHMe_2$), 194 (100, M^+ – SCHMe); mp 112–115 °C dec.

Preparation of [Me$_2$EtCSTi(OCH$_2$CH$_2$)$_3$N]$_2$ (12). Compound **8** (0.28 g, 1.2 mmol) was reacted with 0.12 g (0.15 mL, 1.2 mmol) of 2-methyl-2-butanethiol in THF (30 mL). The suspension was stirred at room temperature for 3 h under an inert atmosphere. The solvent was then removed under vacuum, and the product was dissolved in hot toluene and stored at –25 °C. After 12 h, the pure yellow microcrystalline product was separated in 88% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, 6 H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 1.43 (s, 12 H, $C(CH_3)_2$), 1.65 (q, 4 H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 2.93 (t, 4 H, $^3J_{HH}$ = 7.4 Hz, NCH_2), 3.07–3.12 (m, 4 H, NCH_2), 3.41–3.51 (m, 4 H, NCH_2), 4.58 (t, 4 H, $^3J_{HH}$ = 7.4 Hz, OCH_2), 4.68–4.74 (m, 4 H, OCH_2), 4.82–4.91 (m, 4 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 10.04 (CH_2CH_3), 31.73 ($C(CH_3)_2$), 39.12 (CH_2CH_3), 51.99 ($C(CH_3)_2$), 57.76 (CH_2N), 64.17 (2 C, CH_2N) 73.96 (2 C, CH_2O), 75.50 (CH_2O); IR (Nujol, cm^{-1}) 2955, 2922, 2851, 1459, 1376, 1260, 1069, 1026, 800, 647, 564; MS *m/e* (relative intensity) 297 (10, M^+), 282 (1, M^+ – Me) 268 (20, M^+ – Et), 267 (3, M^+ – 2Me), 276 (1, M^+ – CMe_2Et), 194 (100, M^+ – $SCMe_2Et$); decomposed on heating. Anal. Calcd for $C_{11}H_{23}NO_3STi$: C, 44.45; H, 7.80. Found: C, 44.94; H, 7.87.

Preparation of [PhSTi(OCH$_2$CH$_2$)$_3$N]$_2$ (13). In a 100-mL round-bottomed flask equipped with side arm, **8** (0.38 g, 1.6 mmol) was suspended in 50 mL of THF and 0.16 mL (0.17 g, 1.5 mmol) of benzenethiol was added dropwise. Upon addition of the benzenethiol, the color changed from yellow to bright orange. The reaction was refluxed for 1 h. The solvent was removed and the orange solid crystallized from hot toluene in 85% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (t, 4 H, $^3J_{HH}$ = 5.4 Hz, NCH_2), 3.14–3.22 (m, 4 H, NCH_2), 3.44–3.51 (m, 4 H, NCH_2) 4.58–4.85 (m, 12 H, OCH_2), 6.78–7.12 (m, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 57.26 (NCH_2), 60.29 (2C, NCH_2), 72.99 (2C, OCH_2), 75.98 (OCH_2), 124.07 (*p*-C_6H_5), 127.79 (*o*-C_6H_5), 130.67 (*m*-C_6H_5); IR (Nujol, cm^{-1}) 3100, 3050, 2951, 2922, 2851, 1576, 1461, 1377, 1251, 1091, 1028, 900, 802, 748, 646, 616, 547; MS *m/e* (relative intensity) 303 (9, M^+), 194 (36, M^+ – SPh); mp 113–115 °C with some decomposition. Anal. Calcd for $C_{12}H_{17}NO_3STi$: C, 47.54; H, 5.65. Found: C, 46.86, H, 4.96.

Preparation of [CH$_2$CHCH$_2$STi(OCH$_2$CH$_2$)$_3$N]$_2$ (14). The procedure was the same as for **10** except that the pure compound was obtained after several recrystallizations from CH_2Cl_2/pentane in 45% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (t, 4 H, $^3J_{HH}$ = 5.4 Hz, NCH_2), 3.14–3.21 m, 4 H, NCH_2), 3.46–3.55 (m, 4 H, NCH_2, 4.05 (dd, 4 H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.9 Hz, SCH_2), 4.50 (t, 4 H, $^3J_{HH}$ = 7.2 Hz, OCH_2), 4.56–4.75 (m, 4 H, OCH_2), 4.81–4.88 (m, 2 H, OCH_2), 4.91–4.99 (m, 4 H, CH_2CH), 5.05–5.12 (m, 2 H, CH_2CH), 5.90–6.04 (m, 2 H, $CHCH_2$); ^{13}C (75.4 MHz, $CDCl_3$) δ 38.5 ($SCH_2CH{=}CH_2$), 57.20 (NCH_2), 60.57 (2 C, NCH_2), 72.83 (2 C, OCH_2), 75.97 (OCH_2), 113.34 ($SCH_2CH{=}CH_2$), 139.91 ($SCH_2CH{=}CH_2$); IR (Nujol, cm^{-1}) 2958, 2846, 1457, 1259, 1100, 1075, 1030, 802, 729, 603; MS *m/e* (relative intensity) 267 (1, M^+), 226 (1, M^+ – allyl), 194 (31, M^+ – S(allyl)); mp = 131–132 °C dec.

Preparation of Me$_2$NTi(MeNCH$_2$CH$_2$)$_3$N (15). In 15 mL of THF was dissolved 1.09 g (4.89 mmol) of $Ti(NMe_2)_4$ and 0.92 g (4.89 mmol) of $(HMeNCH_2CH_2)_3N$, and the mixture was heated to 60 °C with stirring for 2 h. The initially yellow solution turned red, and dimethylamine was evolved. The solvent was removed in vacuo and the crude product vacuum distilled (116–120 °C at 0.15 mmHg). A red oil was obtained, which solidified upon standing for several days. All attempts at crystallization have failed. Characterization data for **15**: yield 55%; ^{1}H NMR (C_6D_6) δ 2.59 (t, 6 H, NCH_2), 3.16 (t, 6 H, NCH_2), 3.27 (s, 15 H, NCH_3, $N(CH_3)_2$); ^{13}C NMR: δ 43.63 (CH_3N), 45.43 (CH_3N), 52.51 (CH_2N), 58.75 (CH_2N); HRMS (EI): *m/e* 277.17630 (calcd for $C_{11}H_{27}N_5Ti$ 277.17459; error + 1.53 ppm).

Table I. Crystal Data for Compound **8**

formula	$(TiO_3N_2C_8H_{18})_2$
fw	476.24
space group	$P2_1/c$
a, Å	11.154 (5)
b, Å	10.942 (2)
c, Å	9.708 (5)
α, deg	90.0
β, deg	115.4 (2)
γ, deg	90.0
V, Å^3	1070.3 (8)
Z	2
d_{calc}, g/cm^3	1.478
μ(Mo Kα), cm^{-1}	8.2
data collcn instrum	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
orientation reflcns: no.; range (2θ), deg	25; 21.0 < θ < 30.1
temp, °C	–50 (1)
data collcn range (2θ), deg	4.0–45.0
no. data collcd	2971
no. unique data	1482
tot. no. of data with $F_o^2 > 3\sigma(F_o^2)$	1287
transm factors: max; min (φ-scans)	0.999; 0.971
R;[a] R_w[b]	0.031; 0.059

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

Preparation of *t*-BuOTi(MeNCH$_2$CH$_2$)$_3$N (16). A solution of 0.31 g (4.2 mmol) of *tert*-butyl alcohol in 10 mL of toluene was added dropwise to a solution of 1.00 g (4.5 mmol) of $Ti(NMe_2)_4$ in 10 mL of toluene. After the mixture was stirred at room temperature for 30 min, a solution of 0.80 g (4.3 mmol) of $(HMe_2MCH_2CH_2)_3N$ was added. The reaction mixture was kept at 60 °C for an additional 2 h. The volatiles were removed in vacuo and the crude product was purified by sublimation (twice) at 90–100 °C (0.05 mmHg). The pure product was obtained in 54% yield: ^{1}H NMR (C_6D_6) δ 1.57 (s, 9 H, $(CCH_3)_3$), 2.69 (t, 6 H, NCH_2), 3.15 (t, 6 H, NCH_2), 3.43 (s, 9 H, NCH_3); ^{13}C NMR (C_6D_6) δ 32.89 ($(CH_3)_3C$), 48.45 (CH_3N), 52.87 (CH_2N), 58.47 (CH_2N), 80.21 (CO); HRMS (EI): *m/e* 308.19045 (calcd for $C_{13}H_{30}N_4OTi$ 306.18941; error + 1.78 ppm). Anal. Calcd for $C_{13}H_{30}N_4OTi$: C, 50.9; H, 9.80; N, 18.30. Found: C, 50.53; H, 9.83; N, 18.12.

Preparation of ($C_6H_5CH_2NHCH_2CH_2$)$_3$N. Benzaldehyde (17.5 g, 0.165 mol) was added dropwise to a solution of 7.31 g (0.050 mol) of $N(CH_2CH_2NH_2)_3$ in 50 mL of ethanol at 20 °C. The yellow solution was stirred for 1 h and cooled in an icebath. To this solution was added portionwise 7.2 g (0.19 mol) of $NaBH_4$ at 5–10 °C and the mixture stirred for additional 2 h at room temperature. The reaction mixture was then diluted with 100 mL of water and extracted with 3 × 50 mL of ether. The organic layers were extracted with 2 × 200 mL of 1 N HCl. The HCl layers were washed with 2 × 50 mL of ether, made basic with solid K_2CO_3 to pH > 10, and extracted with 3 × 50 mL of ether. The ether layers were dried over Na_2SO_4 and concentrated in vacuum to give the product as a pale yellow oil in 83% yield. The compound decomposes on attempted distillation (280 °C at 0.01 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.73 (br, s, NH), 2.56 (t, 6 H, CH_2N), 2.65 (t, 6 H, CH_2N), 3.72 (s, 6 H, CH_2N), 7.25 (s, 15 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 47.19 (CH_2N), 54.03 (CH_2N), 54.44 (CH_2N), 126.77, 128.01, 128.30, 140.42 (C_6H_5).

Single-Crystal X-ray Diffraction Study of Me$_2$NTi(OCH$_2$CH$_2$)$_3$N (8). A yellow-colored crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at –50 ± 1 °C. The cell constants for data collection 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 and a correction based on a decay in the standard reflections of 1.9% were applied to the data. An absorption correction based on a series of φ scans was also applied. The agreement factor for the averaging of observed reflections was 1.2% (based on *F*).

The space group $P2_1/c$ was unambiguously determined by systematic absences prior to the solution. The structure was solved by direct methods.[8] The titanium atom and several oxygen atoms were placed in

Table II. Positional Parameters and Their Estimated Standard Deviations for **8**[a]

atom	x	y	z	B, Å²
Ti	0.15274 (3)	0.48091 (4)	0.12541 (4)	1.50 (1)
N(1)	0.1880 (2)	0.5670 (2)	0.3524 (2)	1.81 (4)
C(1)	0.0597 (2)	0.6118 (3)	0.3480 (2)	2.14 (5)
C(2)	−0.0592 (2)	0.5535 (3)	0.2210 (2)	1.99 (5)
O(1)	0.1226 (2)	0.3536 (2)	0.2357 (2)	2.06 (3)
C(3)	0.2810 (2)	0.6686 (2)	0.3725 (2)	2.19 (5)
C(4)	0.2365 (2)	0.7303 (2)	0.2183 (3)	2.40 (5)
O(2)	−0.0386 (1)	0.5553 (2)	0.0864 (2)	1.76 (3)
C(5)	0.2450 (3)	0.4664 (3)	0.4623 (3)	2.34 (6)
C(6)	0.1623 (3)	0.3536 (2)	0.3952 (3)	2.48 (6)
O(3)	0.2079 (1)	0.6396 (2)	0.1066 (2)	2.10 (4)
N(2)	0.3241 (2)	0.4126 (2)	0.1596 (2)	2.32 (5)
C(7)	0.3790 (3)	0.2962 (3)	0.2326 (3)	3.09 (6)
C(8)	0.4158 (3)	0.4716 (3)	0.1129 (4)	3.96 (8)

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

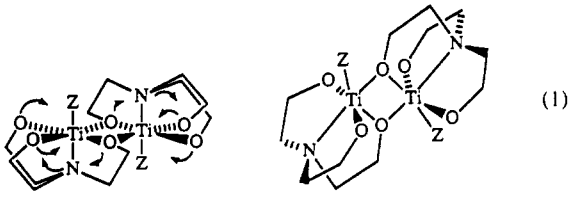
Table III. Important Bond Distances (Å) and Angles (deg) for **8**

	Bond Lengths		
Ti(1)–O(1)	1.873 (1)	Ti(1)–N(1)	2.270 (2)
Ti(1)–O(2)	1.939 (1)	Ti(1)–N(2)	1.943 (2)
Ti(1)–O(2′)	2.160 (1)	Ti(1)–Ti(1′)	3.2547 (6)
Ti(1)–O(3)	1.877 (1)		
	Bond Angles		
N(2)–Ti(1)–O(2′)	179.46 (6)	Ti(1)–O(2)–Ti(1′)	105.01 (5)
O(1)–Ti(1)–O(3)	152.90 (5)	O(2)–Ti(1)–O(2′)	74.99 (5)
N(1)–Ti(1)–O(2)	151.10 (6)		

the model from the *E* map prior to structure factor calculations. The positions of the remaining non-hydrogen atoms were determined by two successive difference Fourier maps. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs.[9] Positional parameters and important bond distances and angles and their estimated standard deviations are given in Tables II and III, respectively.

Discussion

Structural Considerations. Because the stability to temperature variation and the chemical reactivity of dimeric **8** with alcohols and thiols may be closely associated with structural characteristics of the starting titanatrane, we discuss first the main features of the structure of **8**. As seen in the ORTEP drawing of this molecule in Figure 1, its coordination geometry differs substantially from **1** in that the axial Z substituent in the former is trans to an oxygen whereas this substituent is trans to a nitrogen in the latter. Both structures possess a center of symmetry, and the configuration of **8** is seen to be derived from that of **1** by a twisting motion indicated by the curved arrows in transformation (1). In both



(1)

1 (Z = O-*i*-Pr) **8** (Z = Me_2N)

configurations the chelating ligand spans the corners of two adjacent triangular faces of an octahedron. Since the steric requirement of the *i*-Pr group in **1** is similar to that of the Me_2N substituent in **8**, it is plausible to suggest that the more electron-donating Me_2N group prefers to be trans to an alkoxy oxygen rather than the more electron-donating tertiary bridgehead nitrogen. The electron-donating properties of the Me_2N moiety in **8** appear to be enhanced by π-donor bonding to the metal, to the extent that the planarity of this group (sum of the angles = 359.9°) is indicative of this phenomenon. The strong σ-electron-donating ability of the Me_2N group may also be partially reponsible for the lengthening of the trans Ti(1′)–O(2) and Ti(1)–O(2′) linkages, which is compensated by a shortening of the Ti–O (bridging) bonds. Also noteworthy are the short Me_2N–Ti bond lengths (1.943 (2) Å) compared with the C_3N–Ti distances (2.2702 (2) Å) in **8**. Although the metal–metal distance in **8** (3.2547 (6) Å) is shorter than that in **7** (3.290 (2) Å[4]) or in **1** (3.356 (1) Å[1]) there is no need to invoke Ti–Ti bonding.

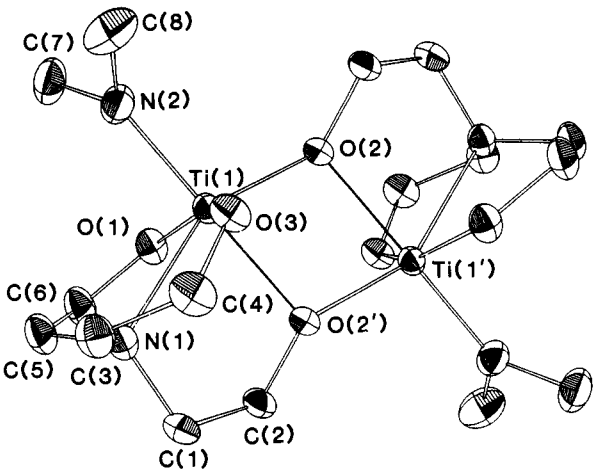
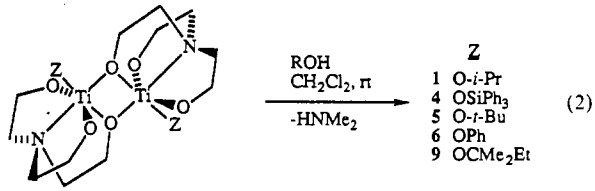


Figure 1. ORTEP drawing of **8**, with ellipsoids drawn at the 50% probability level.

The change in the deployment in the coordination sphere of the ligating atoms in the tetradentate ligand relative to Z in going from **1** to **8** is accompanied by a shortening of the C_3N–Ti bond length (2.333 (1) to 2.270 (2) Å) with concomitant lengthening of the trans Ti–OC link (1.833 (1) to 1.939 (1) Å). The latter bonds in **8** (i.e., Ti(1)–O(2) and O(2′)–Ti(1′) in Figure 1), which serve to connect the halves of the molecule, are considerably shorter than their counterparts in **1** (2.108 (1) Å). The four-membered Ti_2O_2 ring connecting the respective halves of **1** and **8** also display complementarity in the lengths of the other pair of oppositely oriented Ti–O linkages. Thus in **1** these distances are shorter (1.998 (1) Å) while in **8** they are longer (2.160 Å). These observations suggest that the halves of **8** can be described as being bound together by predominantly alkoxy-type bridging bonds, while those of **1** are bridged by predominantly donor–acceptor-like linkages. This structural difference rationalizes the solution thermal stability order **8** > **1** with respect to fluxionality of the dimer halves.[4] Although the Ti–O(bridging) bonds in **8** are short (1.939 (1) Å) they are not as short as the Ti–O (terminal) bonds in **8** (average = 1.875 (1) Å) and **1** (average = 1.864 (1) Å).

Syntheses. Compounds **1**, **4**, **5**, **6**, and **9** are all made from **8** in better than 90% yield via reaction 2. Under the mild conditions of the reaction, the pathway for displacement can be expected



(2)

8 (Z = NMe_2)

to involve nucleophilic attack of an alcoholic oxygen on the metal to form a seven-coordinate intermediate (for which the structure

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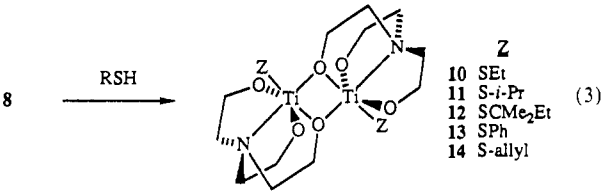
of **7**[4] constitutes corroborating evidence) followed by cleavage of the thermodynamically less stable Ti–NMe_2 bond, elimination of Me_2NH, and twisting of the molecular framework to resemble that of solid-state **1** in the case of **6** (which behaves as a fluxional dimer in solution[4]). In solution, the configurational twist is followed (or perhaps preceded) by dissociation to monomers in the cases of **1**, **4**, **5**, and **9**, which have bulky monodentate substituents on the titanium.

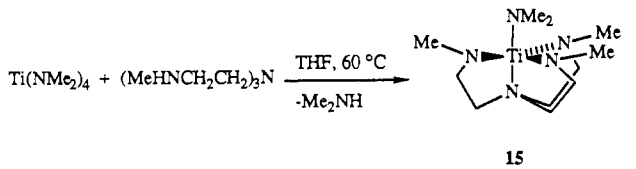
Transformation (3) depicts the reaction of **8** with thiols giving the indicated yellow or orange thiolatotitanatrane dimers in better than 85% yield in most cases. The configuration shown for **10–14** will be justified in the next section.



(3)

Although the displacement of NR_2 from titanium(IV) amides has been previously reported for alcohols,[10] thiols,[11] c-C_5H_6[10] and HC≡CPh,[12] the examples reported here are the first involving the titanatrane structure.

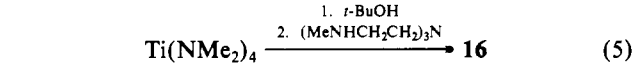
Azatitanatrane **15** is formed in 55% yield as a distillable red oil according to reaction 4. Although this red oil becomes a semisolid upon standing for several days, attempts to recrystallize



15
(4)

this material have so far not been successful. This behavior also appears to be characteristic of $CpTi(NMe_2)_3$.[13] Reaction of $(H_2NCH_2CH_2)_3N$ with $Ti(NMe_2)_4$ gave rise to a soluble complex in THF but all attempts to isolate the product led to insoluble orange materials, from which no oligomeric or monomeric materials could be extracted or sublimed. Evidently in the absence of coordinating solvent, amido or imido bridges can be formed between titanium atoms.[14] Reaction of $(C_6H_5CH_2NHCH_2CH_2)_3N$ with $Ti(NMe_2)_4$ gave rise to decomposition of the tetradentate ligand owing to the strongly basic reaction conditions.[13]

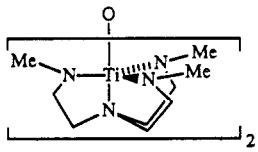
In contrast to the ease of displacement of the Me_2N group in **8** by nucleophiles, **15** upon reaction with *t*-BuOH gave a mixture of starting material, $(t\text{-BuO})_4Ti$, and intermediate alcoholysis products, with no detectable evidence for **16**. Apparently the axial and the equatorial nitrogens in **15** are easily displaced. Compound **16** was, however, synthesized in 54% yield in two steps via reaction 5. The residue from the sublimation gave a ^1H NMR spectrum

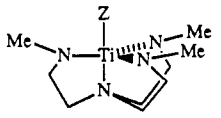


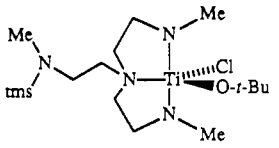
(5)

consistent with the structure shown for **17**, a compound which could arise from partial hydrolysis due to the presence of adventitious water or by thermal decomposition of **16**.

Attempts to displace the Me_2N group of **15** with CpH under a variety of conditions failed. Reactions of $(MeHNCH_2CH_2)_3N$ with $CpTi(NMe_2)_3$ (prepared in situ from $Ti(NMe_2)_4$[13]) under mild conditions did not provide **18**, and heating the reaction mixture led cleanly to the formation of **15**. Steric interactions of a bulky η^5-C_5H_5 group with the upwardly directed Me groups


17


18 Z = Cp
19 Z = Cl


20

on the planar nitrogens in **18**[7,15–17] may preclude formation of this molecule. On the other hand, an η^1 structure may be permitted and further efforts are underway to realize such a compound. The reaction of $CpTi(NMe_2)_3$ with $(H_2NCH_2CH_2)_3N$ gave a red solution in THF, but a black oil formed on standing. Rapid concentration of a red solution formed immediately after reaction gave a red-brown solid that could not be redissolved in THF or benzene. A comproportionation reaction between **15** and $TiCl_4$ aimed at obtaining **19** gave only a brown insoluble product. The reaction of **16** with Me_3SiCl also failed to give **19**, giving instead an oil whose ^1H and ^{13}C NMR spectra are consistent with the sole formation of **20**, a compound similar to the previously reported $N(CH_2CH_2NEt)_2TiCl_2$.[18] Compound **20** does not react further with excess Me_3SiCl nor it does eliminate *t*-$BuOSiMe_3$.[19]

NMR Spectra. As for **1**, **4**, and **5**,[4] the solution ^1H and ^{13}C NMR spectra of the new alkoxy titanatrane **9** are characteristic of monomeric behavior. Compounds **1**, **4**, **5**, and **9** all contain bulky substituents on the upper axial position, thereby inhibiting dimerization. The azatitanatranes **15** and **16** are also consistent with ^1H and ^{13}C NMR spectra of monomeric behavior in solution. Because both **15** and **8** (which is dimeric in solution[4]) possess NMe_2 substituents, the monomeric behavior of **15** in solution can be attributed to the poorer bridging properties of tertiary amino groups and steric shielding of the methyl groups for titanium(IV). This inhibiting influence on dimerization may be accentuated in **16** by the presence of a *t*-BuO group.

The ^1H and ^{13}C NMR behavior of the thiolatotitanatranes **10–14** contrasts with that of the alkoxytitanatranes **1**, **4**, **5**, **6**, and **9** in that all of the former display dimeric behavior in solution from −55 to +55 °C, despite the size of the SR moiety. This suggests a robust dimeric framework which could have the same configuration as **8**. This configuration would be favored by SR substituents since they, like Me_2N groups, are electron donating. Dimeric solution behavior on the part of **10–14** is apparently not inhibited by bulky thiolato groups such as S-*i*-Pr and $SCMe_2Et$ because the alkyl portion is placed well away from the rest of the molecule by the relatively large sulfur atom.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research in the form of a grant to J.G.V. We thank Dr. Victor Young of the Iowa State Molecular Structure Laboratory for his technical assistance in solving the molecular and crystal structure of **8** by X-ray means.

Supplementary Material Available: Tables of crystal data, bond distances, bond angles, hydrogen atom positional parameters, and general displacement parameter expressions and a ball and stick diagram giving the atom numbering (8 pages); a table of structure factors (7 pages). Ordering information is given on any current masthead page.

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